# 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,<sup>1</sup> using the B3LYP functional of Becke and Perdew.<sup>2</sup> The electronic configuration has been described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, and O (SVP)<sup>3</sup> and with the SDD basis and pseudopotential<sup>4</sup> 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 K, 1 bar). Improved electronic energies, obtained from single-point energy calculations using a TZVP basis set<sup>5</sup> on the main atoms, a solvation contribute (PCM model,<sup>6</sup> toluene) and the dispersion corrections<sup>7</sup> (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 **A'**). 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 **B** with respect to **B'** to avoid the sterical interaction between chain and ligand. In **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 C<sub>a</sub>-C of the chain to avoid the sterical contact reported with an arrow (*si* face in C'). For the sake of readability in **b**) the hydrogen atoms of the metallocene skeleton are omitted. With P = polymer chain.

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



**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) kcal/mol are due to steric ligand-monomer interactions ('Pr substituents on phenyl ring, see Chart 1) reported with a dashed red arrow in Figure 2 (**B**). This interaction is also responsible of the larger Hf-N-C angle (122.5 °) reported in **B** with respect to **A** (119.4 °). 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 **A** is due to steric ligand-monomer interaction reported with a dashed red arrow in (**B**). H atoms are omitted for clarity. The preferred 2,1 insertion enantioface (**A**) is the same of the primary insertion reported in Figure 2 **A**, see text.

### **5. References**

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