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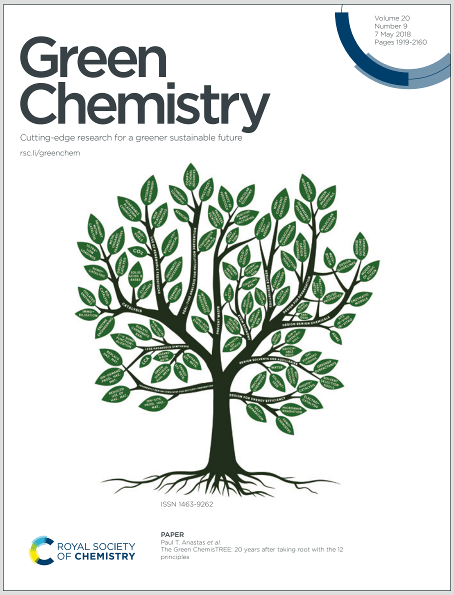

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1. The copolymerization of carbon dioxide (CO_2) and *meso*-epoxides is a promising strategy for utilizing CO_2 as a renewable feedstock, enabling the synthesis of polymeric materials with functional and desirable properties.
2. Enantioselective ring-opening copolymerization (ROCOP) of CO_2 and *meso*-epoxides yields isotactic polycarbonates (iPCs), which are potentially biodegradable and recyclable. These materials offer an eco-friendly alternative to conventional fossil-fuel-based plastics, contributing to the circular economy. This study delves into the critical factors influencing ROCOP enantioselectivity, including: monomer deformation, ligand steric effects modulated by the number and arrangement of chiral centers and noncovalent interactions.
3. A deeper understanding of these selectivity factors could pave the way for designing more efficient catalysts replacing conventional plastics and promoting the utilization of alternative feedstocks. Ultimately, this advances carbon recirculation by transforming CO_2 from a waste product into a valuable resource.

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ARTICLE

Disclosing Multiple Factors Influencing Enantioselective CO_2 and *Meso*-Epoxides Copolymerization with β-Diiminate Zn Catalysts

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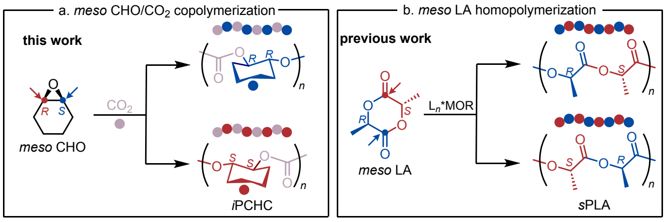
The enantioselective ring-opening copolymerization (ROCOP) of cyclohexene oxide (CHO) and carbon dioxide (CO_2) to produce isotactic poly(cyclohexene carbonate) (*i*PCHC) was systematically investigated using chiral C_1-symmetric zinc β-diiminate (BDI) catalysts. A combination of Density Functional Theory (DFT), molecular steric descriptors ($\%V_{Bur}$), and the activation strain model (ASM) was employed to elucidate the mechanistic pathways and factors governing enantioselectivity. We found that chiral monomeric BDI catalysts exhibit intrinsic enantioselective properties in *meso*-desymmetrization polymerization catalysis, which are significantly enhanced upon formation of dimeric complexes with *anti* and *syn* conformations. The predicted enantioselectivity, arising during the CHO ring-opening step, explains the experimental combination of selected stereocenters on the ligand and preferred stereochemistry of the polymer chain. This study identifies key factors influencing ROCOP enantioselectivity, including monomer deformation, ligand steric effects dictated by the number of chiral centers, and noncovalent interactions, all contributing additively to the observed selectivity. These insights provide a better understanding of the mechanistic origins of enantioselectivity in CHO/CO_2 ROCOP and offer guidance for the design of more efficient catalysts.

Introduction

The use of carbon dioxide (CO_2) to produce commodities has been deeply investigated in recent years. CO_2 is an ideal feedstock because it is nontoxic, inexpensive, abundant on Earth and its consumption could contribute to the mitigation of the global temperature rise.[1] The copolymerization of CO_2 and *meso* epoxides[2,3] represents a viable route since it leads to the formation of polycarbonates (PCs) that are potentially biodegradable and recyclable materials. The inclusion of cyclohexene oxide (CHO) in the polymer backbone overcomes one of the problems associated with most aliphatic polycarbonates such as the low glass transition temperatures (T_g); indeed, poly(cyclohexene carbonate) (PCHC) can reach T_g up to 120°C and tensile modulus ~ 3.6 GPa, enabling its use also as engineering plastic.[4,5] Furthermore, PCHC is chemically recyclable to epoxide and carbon dioxide by using homo- and heterodinuclear catalysts highly active in solid-state depolymerizations.[6-8]

The enantioselective copolymerization of CO_2 and CHO *via* ring-opening copolymerization (ROCOP)[9-13] produces isotactic poly(cyclohexene carbonate) (*i*PCHC), a semicrystalline thermoplastic with physical properties highly dependent on its stereoregularity.[4] Being CHO a *meso* compound displaying two neighboring stereocenters in opposite configurations, the selective ring-opening at one of the two chiral carbons results in the desymmetrization of this monomer and formation of two different repeating units. The attack at *S*- or *R*-configured carbons produces *R,R*- or *S,S*-chain, respectively (Scheme 1a). *Meso*-desymmetrization catalysis is a valuable synthetic approach when selective activation of one stereogenic center is achieved during the catalytic cycle.[14,15] Notable examples include the stereoselective ring-opening polymerization (ROP) of *meso*-lactide (*meso* LA) by chiral aluminum complexes (Scheme 1b). In this process, preferential attack at the carbonyl group adjacent to the *R* or *S* stereogenic center, determined by catalyst chirality, results in the formation of highly syndiotactic poly(lactic acid) (*s*PLA).[16–18] DFT calculations have rationalized this preference,[19] attributing it to repulsive interactions between the ligand and the monomer, which also explain the stereoselective ROP of racemic lactide (*rac*-LA),[20] and the regioselective ROP of 3-methyl glycolide.[21]



Scheme 1 *Meso* desymmetrization catalysis in ROCOP of CHO and CO_2 (a) and in ROP of *meso* LA (b).

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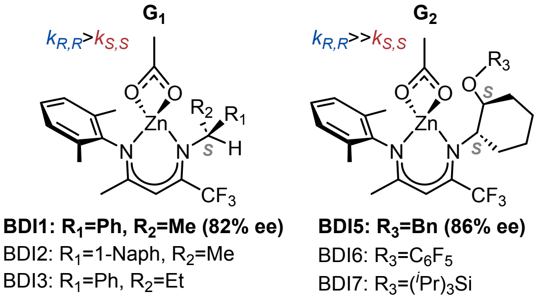
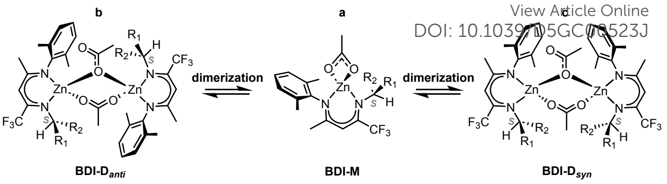
Coates and coworkers reported a series of C_1-symmetric zinc β-diiminate catalysts (**BDI**, Scheme 2) that displayed high activity, carbon linkages and a noteworthy enantioselectivity towards the ROCOP of CO_2 and *meso* CHO.[12] The BDI family having 2,6-dimethylphenyl as N-aryl group have been classified as first (G_1) and second generations (G_2) depending on the number of chiral centers and size of the chiral substituents (see the single *S* stereocenter for G_1 and the two *S* stereocenters for G_2 in Scheme 2). Interestingly, moving from G_1 to G_2 systems, the amplification of the enantioselectivity in the copolymerization of CHO and CO_2 has been obtained.[12d]

Mechanistic studies suggested that, starting from monomeric species (**BDI-M**, Scheme 3a), the CO_2/CHO copolymerization catalyzed by **BDI** systems involves dimeric species (**BDI-D**) that can adopt *anti* (**BDI-D*anti***, Scheme 3b) or *syn* (**BDI-D*syn***, Scheme 3c) conformations.[12] Indeed, X-ray analysis of the catalytic precursor revealed its preferred dimeric structures, with a core consisting of a 6-membered ring containing the two Zn centers, one acetate bridging with both its oxygens in a $k^2\mu$ fashion while the other in a $k^1\mu$ fashion. The **BDI1** complex (Scheme 2) exhibited an *anti* conformation (**BDI1-D*anti***, Scheme 3b), bearing the N-aryl and the *sec*-phenethyl groups on opposite sides of the plane formed by the Zn atoms and the acetate groups.[12] The *syn* conformation (**BDI1-D*syn***, Scheme 3c), bearing the substituents on the same side of the plane, was not observed. We were intrigued by the asymmetric amplification going from G_1 to G_2 generations that are among the most stereoselective reported in literature.[22] At the same time, our initial guess was that chiral **BDI-M** may also show an intrinsic enantioselective character into the *meso* desymmetrization catalysis further amplified by the formation of dimeric species, considered as the active species in solution.[12c] To assess this hypothesis, we used computational methods rooted into the Density Functional Theory (DFT), performing an extensive mechanistic study on the initiation and propagation steps of the CO_2/CHO ROCOP and thorough understanding of the factors affecting the enantioselective copolymerization. The DFT results were combined with a steric molecular descriptor ($\%V_{Bur}$)[23,24] and the Activation Strain Model (ASM)[25,26] analysis to better identify the origin of the enantioselective ROCOP promoted by both **BDI-M** and **BDI-D** species. In the following, we selected **BDI1** (Scheme 2) as prototypical example of the G_1 generation[12d] and we will discuss in the first part the results computed on **BDI1-M** and then in the second part on **BDI1-D**. Finally, we will extend the calculations to the **BDI5** catalyst of G_2 generation (Scheme 2) to check the reliability of our computations with respect to the experimental trend[12d] and to compare our data with recent reports in literature.[27]



Scheme 2 Structures of G_1 and G_2 generations of zinc β-diiminate catalysts for enantioselective ROCOP of CHO and CO_2.[12d]



Scheme 3 Schematic equilibrium of BDI systems with monomeric (**BDI-M**, a), and dimeric (**BDI-D**) species with *anti* (**BDI-D*anti***, b) and *syn* (**BDI-D*syn***, c) conformations.

Computational methods

All DFT calculations and geometry optimizations were performed using the Gaussian16 set of programs,[28] using the B3LYP functional.[29] The electronic configuration has been described using two different layers of basis set: SDD for Zn and SVP for all the atoms[30] for characterization of the stationary points 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 have been obtained from single-point energy calculations using the SDD basis set for Zn and 6-311G(d,p) basis set for all the atoms, with a solvation contribute (PCM model,[31] toluene) and the dispersion corrections (D3BJ).[32] These energies added to the SVP-level thermal corrections are named ΔG in the text. Calculations including D3BJ in geometry optimization as well as different computational approaches have been performed to assess the discrepancies of computational results and for a comparison with the literature (Table S1). The counterpoise corrections of the basis set superposition error (BSSE)[33] have been calculated with the same basis sets used for the energy refining, specifying the number of fragments composing the structure of interest. When we extended our analysis to **BDI5-D** (G_2 generation), we used the computational approach used by Cramer[27] (ωB97XD(SMD)/SDD/6-311G+(d,p)//B3LYP-D3BJ/LANL2DZ/6-31G(d))[34] for the initiation reaction whereas for the propagation steps we fully optimized the chiral chains (Supporting Information, Scheme S1). Details of entropic corrections,[35] ASM, $\%V_{Bur}$ and noncovalent interaction analysis (NCI)[36] and visualization are also reported in the Supporting Information.

Results and discussion

Meso-desymmetrization ROCOP by monomeric BDI1 species

The Gibbs energetic profiles for CO_2/CHO ROCOP initiation and propagation steps promoted by **BDI1-M** are summarized in Fig. 1. The catalytic cycle begins with the coordination of CHO to the Zn center, forming intermediate INT1-M. This is followed by the epoxide ring-opening, driven by the nucleophilic attack of the carbonyl oxygen of the acetate on the electrophilic carbon of the CHO epoxide. The enantioselectivity of the initiation reaction is determined by the Gibbs energetic difference

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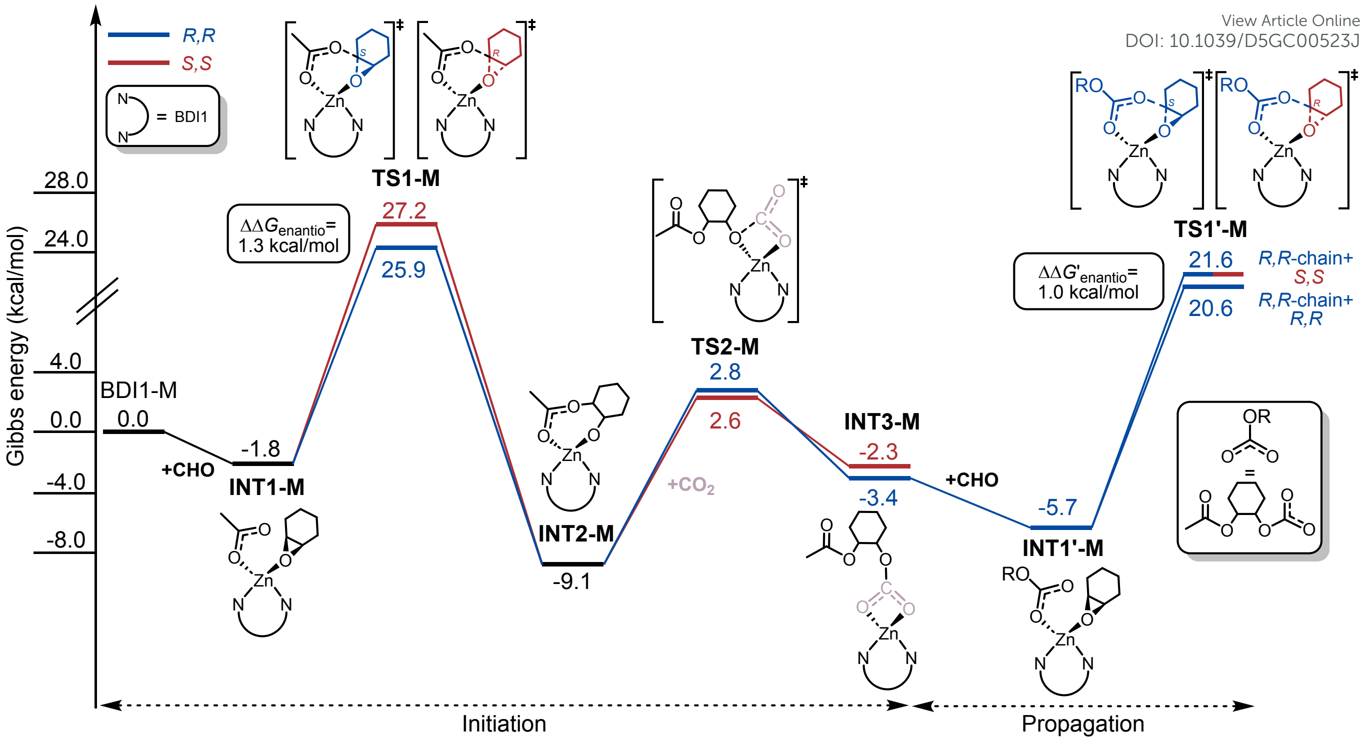

Fig. 1 Gibbs energy profile for initiation and propagation steps in the CHO/CO₂ copolymerization catalyzed by **BDI1-M**. The blue and red pathways correspond to the formation of *R,R*- and *S,S*-configured chains based on attacks on the *S* and *R* carbons of CHO, respectively. The presence of an entire growing unit ((OR)CO_2^-) is simulated in the propagation.

($\Delta\Delta G_{\text{enantio}}$) between the attack on *S* and *R* carbon atoms of CHO as illustrated by TS1-$M_{R,R}$ and TS1-$M_{S,S}$ (depicted with blue and red line in Fig. 1).

Once the ring is opened, intermediate INT2-M is formed. This is followed by an attack of the epoxide oxygen on the electrophilic carbon of CO_2 *via* TS2-M, yielding the thermodynamically stable intermediate INT3-M with a growing polymer chain. The ring-opening of CHO serves as both the rate-determining (rds) and enantioselectivity-determining step, while CO_2 insertion proceeds rapidly. After coordination of a second CHO molecule (INT1′-M), the growing chain ((OR)CO_2^-) is able to selectively attack the latter (TS1′-$M_{R,R}$ and TS1′-$M_{S,S}$). DFT calculations predict the preferential formation of *R,R*-configured repeat units during both initiation and propagation, with $\Delta\Delta G_{\text{enantio}}$ and $\Delta\Delta G'_{\text{enantio}}$ values of 1.3 kcal/mol and 1.0 kcal/mol, respectively (Fig. 1). These results are in line with experimental findings, supporting our initial hypothesis that chiral monomeric Zn(BDI) species exhibit inherent enantioselectivity in *meso*-desymmetrization catalysis. However, the calculated enantioselectivities are lower than those observed experimentally during the ROCOP of CO_2 and CHO.

To further explore the influence of chain chirality, we modeled also the propagation step with the *S,S*-configured unit as growing chain. DFT results (Fig. S1) confirm the modest enantioselectivity imparted by **BDI1-M**, regardless of the chirality of the last inserted unit.

To clarify the origin of **BD1-M** enantioselectivity, we employed the ASM analysis[25] combined with the steric maps of % buried volume analysis (%V_{Bur}).[23] ASM quantifies the strain energy (ΔE_{Strain}) required to deform the two interacting fragments - the catalyst precursor and growing chain ($\Delta E_{\text{Strain(Cat+chain)}}$) and the monomer ($\Delta E_{\text{Strain(Mon)}}$) - from their optimal geometries into the conformations required for the reaction. We successfully applied such combined approach for understanding the origin of stereoselective α-olefin polymerization transition metal catalyzed[37] as well as the ROP of *rac*-LA.[38] The fragmentation approach used for the ROCOP is illustrated in Fig. S2 and detailed methodologies are provided in the Supporting Information.

The $\Delta\Delta E_{\text{Strain}}$ values (Table 1) for the two competing attack pathways on CHO indicate that the primary contributor to enantioselectivity is the monomer deformation energy ($\Delta E_{\text{Strain(Mon)}}$). The latter favors attack on the *S* carbon of CHO over the *R* carbon during both the initiation (TS1-$M_{R,R}$ and TS1-$M_{S,S}$) and propagation (TS1′-$M_{R,R}$ and TS1′-$M_{S,S}$) steps.

The inherent structural differences in the deformation energy required for the *S* and *R* pathways appear to be the main driver

Table 1 ASM results for selected TSs leading the enantioselectivity of the initiation and propagation steps for ROCOP of CO_2 and CHO promoted by **BDI1-M**.

Initiation	TS1-$M_{R,R}$	TS1-$M_{S,S}$	$\Delta\Delta E$[a]
ΔE_{Strain}	64.4	70.4	6.0
$\Delta E_{\text{Strain(Cat+chain)}}$	32.9	32.0	-1.0
$\Delta E_{\text{Strain(Mon)}}$	31.4	38.4	**7.0**
Propagation	TS1′-$M_{R,R}$	TS1′-$M_{S,S}$	$\Delta\Delta E$
ΔE_{Strain}	67.6	74.4	6.7
$\Delta E_{\text{Strain(Cat+chain)}}$	35.0	32.5	-2.5
$\Delta E_{\text{Strain(Mon)}}$	32.6	41.8	**9.2**

[a] $\Delta\Delta E$ values (kcal/mol) calculated as the difference between each ΔE term for TS1-M leading to *S,S*- and *R,R*-chain.

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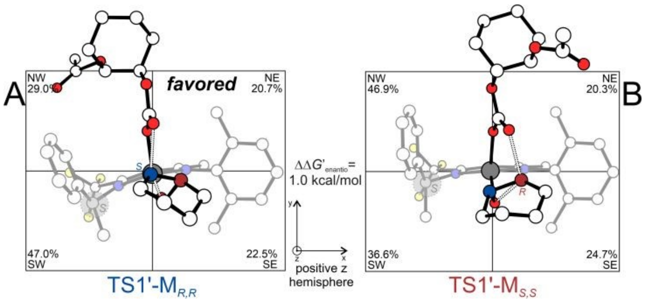

Fig. 2 DFT optimized geometries for TS1'-M with the attack to *S* (A) and *R* (B) CHO stereocenters with the steric maps calculated by $\%V_{\text{Bur}}$ for the propagation step promoted by **BDI1-M** with *R*,*R*-configured repeat units.

of the observed enantioselectivity of **BDI1-M**. A detailed examination of the competitive TS structures (Fig. 2) using a modified $\%V_{\text{Bur}}$ analysis,[23,24] specifically designed to visualize octant occupancies (Fig. S3), provides further insight into the origins of **BDI1-M** enantioselectivity.

In the pathway involving attack on the *S* carbon of CHO, the monomer preferentially occupies the unencumbered southeast (SE) octants (Fig. 2A). This orientation maintains a larger distance (4.6 Å) between the monomer and the chiral carbon of the N-aryl imines in the ligand. Conversely, the attack on the *R* carbon of CHO results in a closer proximity (4.4 Å) between these two atoms, as shown in Fig. 2B.

This closer interaction forces part of the ligand to tilt, resulting in the occupation of the more congested southwest (SW) and northwest (NW) quadrants.

We can argue that this effect is mainly due to the interaction between the chirality of the ligand and the stereogenic centers of monomer whereas the chirality of the growing chain plays a limited effect. Indeed, this feature is similar for initiation and propagation steps and the ASM results (Table 1) combined with the $\%V_{\text{Bur}}$ steric maps (Fig. 2 and Fig. S4) support this interpretation.

Meso-desymmetrization ROCOP by dimeric BDI1 species

After unveiling the enantioselective features of **BDI1-M**, we investigated the initiation and propagation cycles for the catalytic species in its dimeric form (**BDI1-D**). Several mechanistic studies have suggested that the dimeric forms act as the active species in this reaction, as they are considered kinetically more feasible.[12,39,40]

We calculated, at first, the Gibbs energies for the formation of the *anti* and *syn* dimeric species (**BDI1-D*anti*** and **BDI1-D*syn***) corrected by BSSE (ΔG_{dim}). The **BDI1-D*anti*** (ΔG_{dim} = -11.0 kcal·mol^{-1}) is more stable than **BDI1-D*syn*** (ΔG_{dim} = -5.9 kcal·mol^{-1}) by around 5 kcal·mol^{-1} (Fig. S5). This finding is consistent with prior X-ray structural data of the catalyst[12d] and earlier calculations on zinc pyridylamido ligands.[40]

The reaction pathways for the initiation step of ROCOP of CHO and CO_2 catalyzed by **BDI1-D*anti*** (solid line) and **BDI1-D*syn*** (dashed line) are presented in Fig. 3 (separate profiles in Fig. S6–S7).

Gibbs energies are referenced to the most stable species, **BDI1-D*anti*** + CHO (adding CO_2 after INT2-D). The catalytic attack by the carbonyl oxygen of acetate on the *S* stereocenter of CHO, following coordination, is energetically favored, resulting in the formation of a *R,R*-chain, consistent with experimental observations.[12] Although the activation energies for **BDI1-D*anti*** and **BDI1-D*syn*** are comparable when referenced to the most stable precursor (**BDI1-D*anti*** + CHO), **BDI1-D*syn*** exhibits lower activation energies when considered against its suitable reference point (Fig. 3). After we computed direct CO_2 insertion on the dimeric species, we also hypothesized the dissociation of a catalyst unit with formation of the monomeric INT2-M and following CO_2 insertion (TS2-M), as hypothesized experimentally and computationally (Fig. 3, grey color).[12d,27] However, the greater stability of the dimeric species results also in lower barriers for CO_2 insertion (compare TS2-D with TS2-M in Fig. 3). This agrees with experimental evidence that **BDI1** forms a tightly bound dimer, in contrast to the more labile **BDI5** complex[12d] and the higher dissociation energy of **BDI1-D** contributes to the elevated energy of INT2-M (10.2 kcal·mol^{-1}). In any case, *both* **BDI1-D*anti*** and **BDI1-D*syn*** exhibit enantioselectivity during the initiation step, leading to the formation of *R,R*-chains as observed experimentally. Furthermore, both dimers amplify enantioselectivity compared to the monomeric species (Fig. 3 vs. Fig. 1), underscoring the role of dimerization in the amplification of the enantioselectivity.

The ASM analysis reported in Table 2 confirms the pivotal role played by the monomer deformation ($\Delta E_{\text{Strain(Mon)}}$) in destabilizing the attack at the *R*-configured carbon (TS1-D$_{S,S}$ *vs.* TS1-D$_{R,R}$). Indeed, the $\Delta\Delta E_{\text{Strain(Mon)}}$ difference is the main feature responsible for the enantioselectivity of the initiation step promoted by both **BDI1-D*anti*** and **BDI1-D*syn*** (values in bold in Table 2, 4.6 and 4.7 kcal·mol^{-1}, respectively).

The DFT geometries of the relevant TSs along with the $\%V_{\text{Bur}}$ steric maps derived from the octant occupancies are reported in Fig. 4. The dimeric active site species shifts the CHO in the more occupied NW and SW octants with respect to **BDI1-M** (Fig. S4) and this higher occupancy increases the enantioselectivity for both **BDI1-D*anti*** and **BDI1-D*syn*** species.

Table 2 ASM results for selected TSs leading the enantioselectivity of the initiation and propagation steps for ROCOP of CO_2 and CHO promoted by **BDI1-D**.

	anti			*syn*		
Initiation	TS1-D$_{R,R}$	TS1-D$_{S,S}$	$\Delta\Delta E$	TS1-D$_{R,R}$	TS1-D$_{S,S}$	$\Delta\Delta E^a$
ΔE_{Strain}	83.1	89.2	6.1	79.0	85.3	6.3
$\Delta E_{\text{Strain(Cat+chain)}}$	62.6	64.1	1.5	57.9	59.6	1.6
$\Delta E_{\text{Strain(Mon)}}$	20.5	25.1	**4.6**	21.1	25.8	**4.7**
Propagation	TS1'-D$_{R,R}$	TS1'-D$_{S,S}$	$\Delta\Delta E$	TS1'-D$_{R,R}$	TS1'-D$_{S,S}$	$\Delta\Delta E$
ΔE_{Strain}	78.3	85.0	6.7	72.1	73.5	1.4
$\Delta E_{\text{Strain(Cat+chain)}}$	54.2	55.0	0.8	47.5	48.4	0.9
$\Delta E_{\text{Strain(Mon)}}$	24.1	30.0	**5.9**	24.6	25.1	**0.5**

[a] $\Delta\Delta E$ values (kcal/mol) calculated as the difference between each ΔE term for TS1-D$_{S,S}$ and TS1-D$_{R,R}$.

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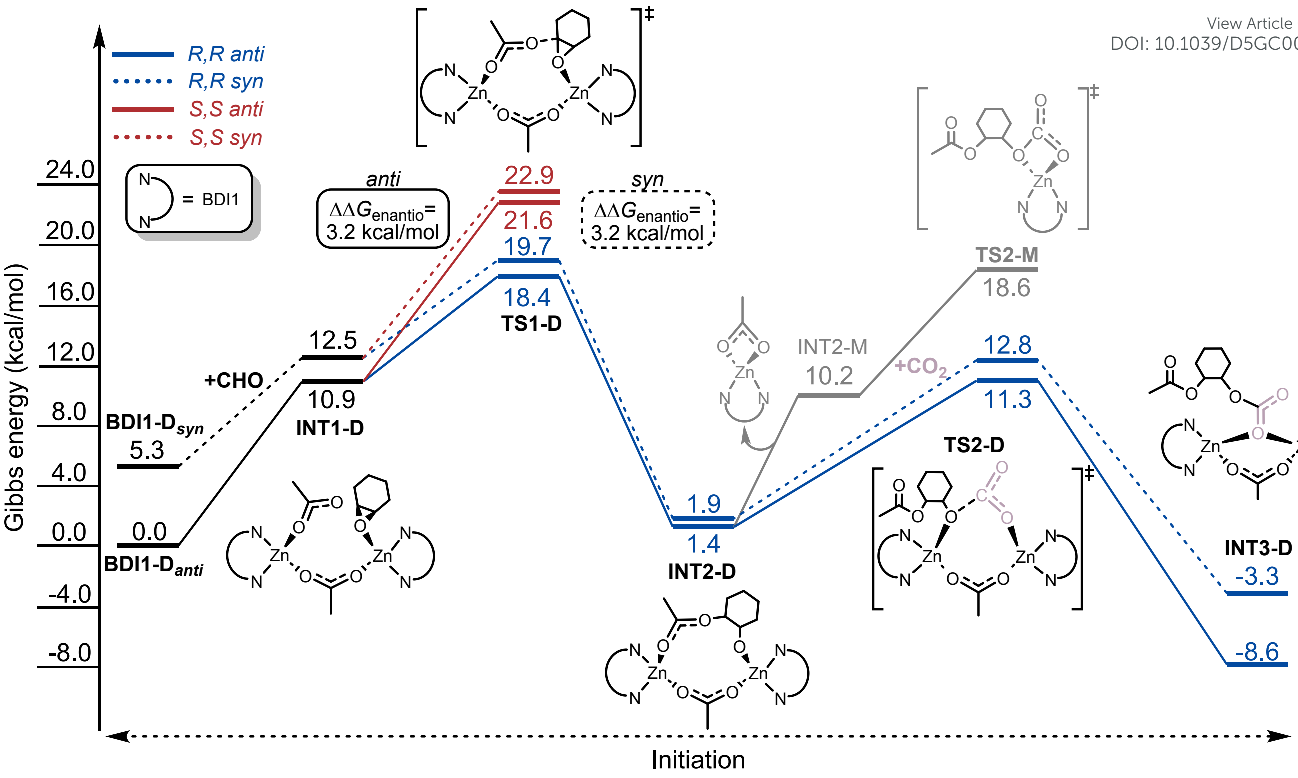

Fig. 3 Gibbs energy profile of the initiation reaction for CHO and CO$_2$ ROCOP involving **BDI1-D*anti*** (full line), **BDI1-D*syn*** (dashed line) and **BDI1-M** (in grey) species. Energies (kcal/mol) are calculated with respect to the most stable **BDI1-D*anti*** species. The paths leading to the formation of *R,R*-chain and *S,S*-chain are reported in blue and red, respectively.

To complete our understanding of the key factors inferring the ROCOP enantioselectivity, we included also the propagation step, thus simulating the presence of an entire repeating unit (Supporting Information for details, Scheme S1). Both **BDI1-D*anti*** and **BDI1-D*syn*** were considered, and Fig. 5 reports the minimum energy path of the propagation for **BDI1-D** having an *R,R*-configured growing chain. The analogous results for **BDI1-D** species bearing a *S,S*-configured growing chain are reported in Fig. S8. The activation barriers of **BDI1-D*syn*** are comparable to those of the **BDI1-D*anti*** species if calculated with respect to the most stable INT3-D$_{anti}$, but sensibly lower if the suitable reference INT3-D$_{syn}$ is considered. Finally, the enantioselectivity of *both* species is confirmed, with a strong tendency for formation of *R,R*-chain with respect to *S,S*-chain (2.9 and 4.0 kcal·mol^{-1}, Fig. 5).The ASM analysis on the **BDI1-D** propagating species (Table 2, propagation) confirmed that the $\Delta E_{\mathrm{Strain(Mon)}}$ is the main factor leading to the favored attack on the *S*-configured carbon for **BDI1-D*anti*** (5.9 kcal·mol^{-1} higher than TS1-D$_{R,R}$, Table 2). For **BDI1-D*syn***, the picture is less straightforward revealing that the strain energetic variation of both fragments is less dominant. The steric maps analysis (Fig. 6) revealed that, for **BDI1-D*anti***, the TS1-D$_{R,R}$ displays lower %V_{Bur} of the octants around the monomer (NW 33.7% and SW 42.1%) compared to TS1-D$_{S,S}$, in which the monomer is again shifted towards the SW octant. For **BDI1-D*syn***, occupancy of SW quadrant in TS1-D$_{S,S}$, where the monomer is mainly located, is higher than in TS1-D$_{R,R}$

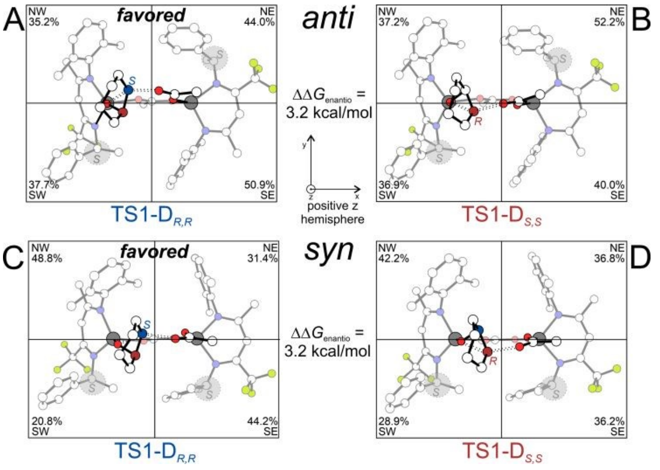

Fig. 4 DFT geometries and %V_{Bur} (octants) of the rds of **BDI1-D*anti*** (A and B) and **BDI1-D*syn*** (C and D) species for the initiation of the ROCOP of CO$_2$ and CHO.

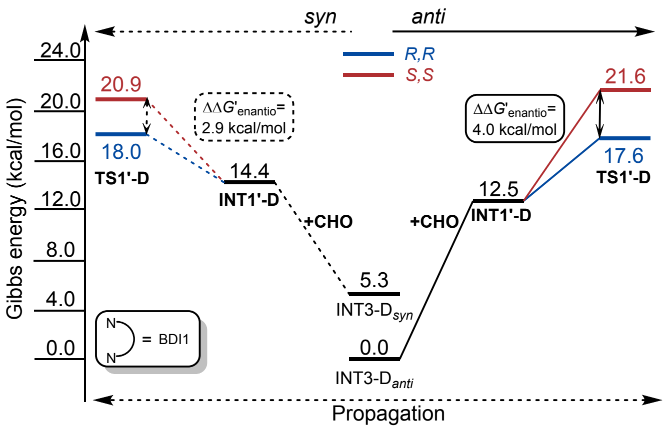

Fig. 5 Gibbs energy profile for the CHO ring-opening on a *R,R*-configured growing unit, by **BDI1-D*syn*** (left) and **BDI1-D*anti*** (right). Energies (kcal/mol) calculated with respect to the more stable INT3-D$_{anti}$ species. The paths leading to a second *R,R*- and *S,S*-chain formation are reported respectively in blue and red.

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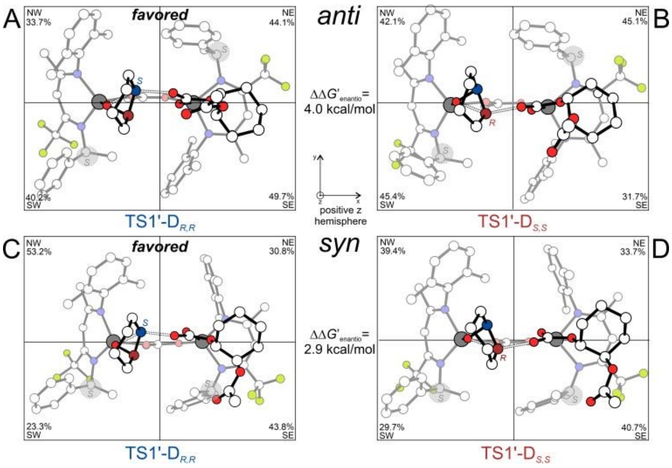

Fig. 6 DFT geometries and %V_{Bur} (octants) of the rds of **BDI1-D*anti*** (A and B) and **BDI1-D*syn*** (C and D) species for the propagation of the ROCOP of CO_2 and CHO.

(29.7% vs. 23.3%) but the monomer is partially shifted into the more open NW quadrant.

After careful analysis of the DFT geometries of propagation TSs, we noticed some short distances between hydrogen atoms of the growing chain and fluorine atoms of the -CF_3 group of the ligand for the preferred TS1'-D$_{syn\text{-}R,R}$. The appearance of a green region of the isosurface between the ligand and the growing chain mentioned above by performing NCI analysis (Supporting Information), indicates the presence of a weak, attractive interaction (Fig. 7). This interaction, missing in the initiation step, contributes to the stabilization of TS1'-D$_{syn}$ and highlights the importance of optimizing a complete growing unit in the propagation. As a final check, we also computed the model system by replacing the -CF_3 substituents with -CH_3 and, accordingly, we calculated a lower enantioselectivity (2.0 versus 2.9 kcal/mol, see Fig. S9).

Noncovalent interactions have previously been proposed in the literature to explain the living olefin polymerization character of Ti-based systems[41] and the heterotactic microstructure of *rac*-LA ROP catalyzed by aluminum systems.[42] However, they have not been reported, to the best of our knowledge, as a factor contributing to the enantioselectivity of the ROCOP. Incidentally, the NCI presence might also explain the ASM results of Table 2 where the minor contribution of the ΔE_{Strain} was revealed in particular for the propagation of **BDI1-D*syn*** species.

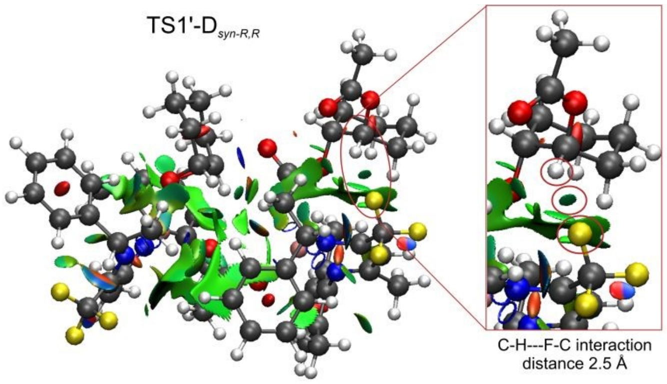

Fig. 7 Gradient isosurface for the TS1'-D$_{syn\text{-}R,R}$. A zoom of the interaction of interest is reported on the right.

Meso-desymmetrization amplification moving from G_1 to G_2 Zn(BDI) species

The last question we want to address in this work is the *meso*-desymmetrization amplification reported for modified **BDI** systems belonging to the G_2 generation. It must be recalled that a computational study on the ROCOP promoted by **BDI5** (Scheme 2) has been reported recently by Cramer.[27] This work proposed the participation of the catalyst in both di- (**BDI5-D)** and mononuclear (**BDI5-M)** forms to the reaction, with the former responsible for CHO ring-opening and the latter for CO_2 insertion. The ROCOP promoted by **BDI5-D** was modelled in the initiation reaction by considering the **BDI5-D*syn*** conformation and the enantioselectivity was ascribed to the ligand distortion energies of the two competing TSs involving the epoxide ring-opening. We extended our analysis to **BDI5-D*syn*** simulating not only the initiation (as in the work of Cramer) but also the propagation steps. For the sake of comparison and to be consistent with the previous work, we used the same computational protocol methods reported by Cramer (variation results depending on the computational protocol are reported in Table S1). Our DFT calculations confirmed the lower enantioselectivity performed by **BDI1-D*syn*** with respect to **BDI5-D*syn*** (Table 3).

The monomer deformation and steric hindrance exerted by the chiral ligand scaffold are crucial for enhancing the enantioselectivity of CHO *meso*-desymmetrization moving from G_1 to G_2 systems. Specifically, the two rds for the propagation at **BDI5-D*syn*** exhibit specular occupancies of the octants located in the north portions versus the ones in the south (Fig. 8). This is an evidence of a strong deformation of **BDI5-D*syn*** occurring in the two TSs (especially for TS1-D$_{S,S}$, as confirmed also by ASM analysis ($\Delta\Delta E_{Strain(Cat+chain)}$ = 1.9 kcal·mol^{-1}, Table S2), but also of the capability of this system to accommodate the reactants. Indeed, we reasoned that although **BDI5-D*syn*** is sterically more hindered around the monomer, it is also more flexible than **BDI1-D*syn***. This is evident by looking at the optimized structure and by comparing the %V_{Bur} of the octants involved (SW and NW) among **BDI1-D*syn*** (Fig. 6 C/D) and **BDI5-D*syn*** (Fig. 8 A/B).

For **BDI1-D*syn***, the steric hindrance exerted during the TSs is always localized more in the NW octants than the SW (respectively, 53.2% vs 23.3% for TS1-D$_{R,R}$, Fig. 6C, and 39.4% vs 29.2% for TS1-D$_{S,S}$, Fig. 6D). For **BDI5-D*syn***, the steric hindrance "switches" between NW and SW depending on the TS: in TS1-D$_{R,R}$, the %V_{Bur} NW-SW are 58.5% and 33.3% respectively, (Fig. 8A), whereas in TS1-D$_{S,S}$ the %V_{Bur} NW-SW are 28.4% and 62.0% respectively (Fig. 8B).

Table 3. Calculated enantioselectivity for the initiation and propagation steps of **BDI1-D*syn*** and **BDI5-D*syn*** at the same level of theory reported in literature.[27]

	BDI1-D*syn*		**BDI5-D*syn***	
	Initiation	Propagation	Initiation	Propagation
$\Delta\Delta G_{enantio}$ (kcal·mol^{-1})	4.3	2.1	4.5	3.5

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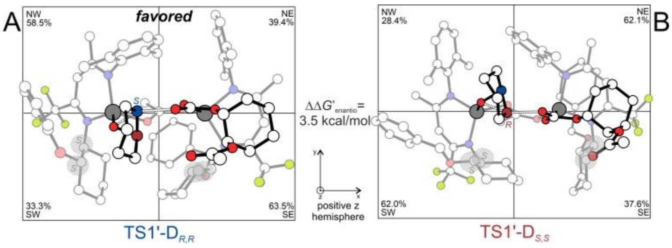

Fig. 8 DFT geometries and $\%V_{Bur}$ (octants) of the rds for the propagation of the ROCOP of CO_2 and CHO at **BDI5-D*syn***.

Conclusions

DFT calculations, combined with ASM analysis and $\%V_{Bur}$ steric maps, provided important insights into the ring-opening copolymerization mechanisms of cyclohexene oxide and carbon dioxide catalyzed by zinc β-diiminate complexes. We claim that the high experimental enantioselectivity reported on the ROCOP of CO_2 and CHO by **BDI** complexes is a synergic addition of multiple factors. Chiral zinc monomeric species, although not actively involved in polymerization, already show an intrinsic enantioselective character in the *meso*-desymmetrization ROCOP leading to the *R,R*-configured growing chain experimentally traced. This intrinsic property offers a simpler modeling approach for predicting catalyst modifications, being the modeling of the mononuclear species far less time consuming.[43] The formation of dimeric species in both *anti* or *syn* conformation amplifies the CHO ring-opening enantioselectivity and increases the preference for the attack at the *S*-configured carbon leading to the *R,R*-growing unit formation. Overall, the enantioselectivity origin of **BDI** catalysts is ascribable to several factors. In both initiation and propagation steps, the monomer deformation, which is a direct consequence of the steric hindrance of the ligand, has been sorted out as the key source of stereoselectivity. Computation of the propagation step with a chiral growing chain revealed the presence of non-covalent interaction between an H atom of the aliphatic bone and fluorine atoms of the ligand contributing to the enantioselectivity. Finally, by a direct comparison between **BDI1-D**, belonging to the first generation, and **BDI5-D**, belonging to the second generation, we reasoned that the origin of the enhanced stereoselectivity for G_2 can be attributed to the enhanced flexibility of the catalyst having two chiral centers suitably positioned on the ligand framework. Revealing the effects contributing to the *meso*-desymmetrization catalysis and their additive rules could be a viable route for the synthesis of biodegradable material with tailored properties competing with the traditional plastics.[44]

Author contributions

Y. Rusconi: investigation, conceptualization, writing, reviewing and editing. M. C. D'Alterio: methodology, conceptualization, writing, reviewing and editing. C. De Rosa: reviewing, editing and supervision. G. W. Coates: reviewing and supervision. G. Talarico: conceptualization, writing, reviewing, editing and supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including Tables S1-S2, Scheme S1, Fig. S1-S9 and cartesian coordinates of the structures discussed are available at https://doi.org/DOI.

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References

1 J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434-504.
2 Y. Wang and D. J. Darensbourg, *Coord. Chem. Rev.*, 2018, **372**, 85-100.
3 Z. Guo, Y. Hu, S. Dong, L. Chen, L. Ma, Y. Zhou, L. Wang and J. Wang, *Chem Catalysis*, 2022, **2**, 519-530.
4 M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1704302.
5 C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman and D. J. Darensbourg, *Polymer*, 2001, **42**, 3995-4004.
6 6 T. M. McGuire, A. C. Deacy, A. Buchard and C. K. Williams, *J. Am. Chem. Soc.*, 2022, **144**, 18444-18449.
7 F. N. Singer, A. C. Deacy, T. M. McGuire, C. K. Williams and A. Buchard, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201785.
8 M. L. Smith, T. M. McGuire, A. Buchard and C. K. Williams, *ACS Catal.*, 2023, **13**, 15770-15778.
9 Catalysts for enantioselective copolymerization of *meso*-epoxides see: (*a*) Y. Liu, W.-M. Ren, J. Liu and X.-B. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 11594-11598; (*b*) B.-H. Ren, Y.-Q. Teng, S.-N. Wang, S. Wang, Y. Liu, W.-M. Ren and X.-B. Lu, *ACS Catal.*, 2022, **12**, 12268-12280.
10 For mechanistic insights see: (*a*) K. Nakano, T. Kamada and K. Nozaki, *Angew. Chem., Int. Ed.*, 2006, **45**, 7274-7277; (*b*) K. Nakano, T. Hiyama and K. Nozaki, *Chem. Commun.*, 2005, 1871-1873. (*c*) K. Nakano, K. Nozaki and T. Hiyama, *J. Am. Chem. Soc.*, 2003, **125**, 5501-5510.
11 J. Huang, J. C. Worch, A. P. Dove and O. Coulembier, *ChemSusChem*, 2020, **13**, 469-487.
12 For experimental works on zinc β-Diiminate catalysts see: (*a*) M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018-11019; (*b*) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738-8749; (*c*) D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911-11924; (*d*) W. C. Ellis, Y. Jung, M. Mulzer, R. Di Girolamo, E. B. Lobkovsky and G. W. Coates, *Chem. Sci.*, 2014, **5**, 4004-4011.
13 M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe and G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129-8152.
14 Á. Enríquez-García and E. P. Kündig, *Chem. Soc. Rev.*, 2012, **41**, 7803-7831.
15 X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, *Chem. Rev.*, 2016, **116**, 7330-7396.

View Article Online
DOI: 10.1039/D5GC00525J

16 T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 4072-4073.

17 T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326.

18 R. Hador, M. Shuster, V. Venditto and M. Kol, *Angew. Chem., Int. Ed.*, 2022, **61**, e202207652.

19 M. C. D'Alterio, C. De Rosa and G. Talarico, *Chem. Commun.*, 2021, **57**, 1611-1614.

20 M. C. D'Alterio, C. De Rosa and G. Talarico, *ACS Catal.*, 2020, **10**, 2221-2225.

21 Y. Rusconi, M. C. D'Alterio, C. De Rosa, Y. Lu, S. M. Severson, G. W. Coates and G. Talarico, *ACS Catal.*, 2024, **14**, 318-323.

22 G.-W. Yang, R. Xie, Y.-Y. Zhang, C.-K. Xu and G.-P. Wu, *Chem. Rev.*, 2024, **124**, 12305-12380.

23 L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nat. Chem.*, 2019, **11**, 872-879.

24 L. Falivene, L. Cavallo and G. Talarico, *ACS Catal.*, 2015, **5**, 6815-6822.

25 F. M. Bickelhaupt and K. N. Houk, *Angew. Chem., Int. Ed.*, 2017, **56**, 10070-10086.

26 P. Vermeeren, S. C. C. van der Lubbe, C. Fonseca Guerra, F. M. Bickelhaupt and T. A. Hamlin, *Nat. Protoc.*, 2020, **15**, 649-667.

27 H. Shao, Y. Reddi and C. J. Cramer, *ACS Catal.*, 2020, **10**, 8870-8879.

28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. C.01. Wallingford, CT, 2016.

29 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

30 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571-2577.

31 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.

32 S. Grimme, *J. Comput. Chem.*, 2004, **12**, 1463-1473.

33 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.

34 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620.

35 L. Falivene, V. Barone and G. Talarico, *Mol. Catal.*, 2018, **452**, 138-144.

36 J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625-632.

37 For the application of ASM analysis on the α-olefin polymerization transition metal catalyzed see: (*a*) E. Romano, V. Barone, P. H. M. Budzelaar, C. De Rosa and G. Talarico, *Chem. Asian J.*, 2024, **19**, e202400155; (*b*) A. Cicolella, E. Romano, V. Barone, C. De Rosa and G. Talarico, *Organometallics*, 2022, **41**, 3872-3883; (*c*) E. Romano, P. H. M. Budzelaar, C. De Rosa and G. Talarico, *J. Phys. Chem. A*, 2022, **126**, 6203-6209; (*d*) F. Núñez-Zarur and A. Comas-Vives, *J. Phys. Chem. C*, 2022, **126**, 296-308; (*e*) Y. Zhao, X. Xu, Y. Wang, T. Liu, H. Li, Y. Zhang, L. Wang, X. Wang, S. Zhao and Y. Luo, *RSC Adv.*, 2022, **12**, 21111-21121.

38 For the application of ASM analysis on the ROP of LA see: (*a*) M. C. D'Alterio, S. Moccia, Y. Rusconi, C. De Rosa and G. Talarico, *Catal. Sci. Technol.*, 2024, **14**, 5624-5633; (*b*) S. Moccia, M. C. D'Alterio, E. Romano, C. De Rosa and G. Talarico, *Macromol. Rapid Commun.*, 2025, **46**, 2400733.

39 J. González-Fabra, F. Castro-Gómez, A. W. Kleij and C. Bo, *ChemSusChem*, 2017, **10**, 1233-1240.

40 I. D'Auria, M. C. D'Alterio, G. Talarico and C. Pellecchia, *Macromolecules*, 2018, **51**, 9871-9877.

41 For selected reports on the noncovalent interaction on olefin polymerization see: (*a*) M. Mitani, T. Nakano and T. Fujita, *Chem. Eur. J.*, 2003, **9**, 2396-2403; (*b*) K. P. Bryliakov, E. P. Talsi, H. M. Möller, M. C. Baier and S. Mecking, *Organometallics*, 2010, **29**, 4428-4430; (c) M. P. Weberski, C. Chen, M. Delferro, C. Zuccaccia, A. Macchioni and T. J. Marks, *Organometallics*, 2012, **31**, 3773-3789; (*d*) C.-C. Liu and M. C. W. Chan, *Acc. Chem. Res.*, 2015, **48**, 1580-1590; (e) G. Talarico and P. H. M. Budzelaar, *Organometallics*, 2016, **35**, 47-54; (*f*) L. Falivene, L. Cavallo and G. Talarico, *Mol. Catal.*, 2020, **494**, 111118; (*g*) Y. Cornaton and J.-P. Djukic, *Acc. Chem. Res.*, 2021, **54**, 3828-3840;

42 S. Gesslbauer, R. Savela, Y. Chen, A. J. P. White and C. Romain, *ACS Catal.*, 2019, **9**, 7912-7920.

43 Z. Cao, L. Falivene, A. Poater, B. Maity, Z. Zhang, G. Takasao, S. B. Sayed, A. Petta, G. Talarico, R. Oliva and L. Cavallo, *Cell Rep. Phys. Sci.*, 2025, 6, 102348.

44 J. W. Han, F. Hollmann, R. Luque, I. K. Song, G. Talarico, T. Tatsumi and N. Yan, *Mol. Catal.*, 2022, **522**, 112233.

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Data availability

Data for this article, including additional computational details, Tables S1-S2, Scheme S1, Fig. S1-S9 and cartesian coordinates (xyz) of the structures discussed are available free of charge at https://doi.org/DOI.