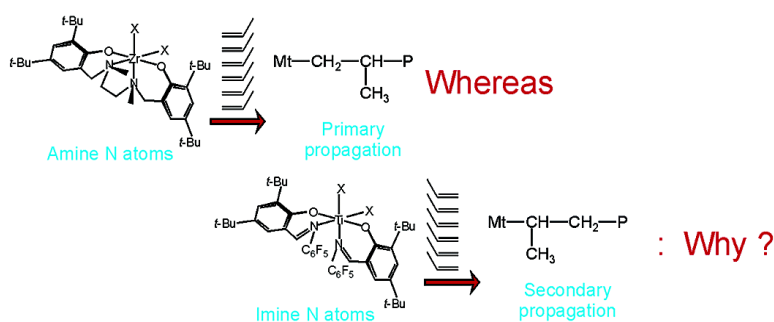


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J. Am. Chem. Soc., **2003**, 125 (24), 7172-7173 • DOI: 10.1021/ja029604o • Publication Date (Web): 21 May 2003

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Origin of the Regiochemistry of Propene Insertion at Octahedral Column 4 Polymerization Catalysts: Design or Serendipity?

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“Catalyst design”, meaning the *rational* invention of a well-defined active species for a targeted application, is often associated with the metallocene¹ and post-metallocene² breakthroughs in stereoselective olefin polymerization. The rapid and apparently endless implementation of new catalysts, leading to an amazing variety of largely unprecedented homopolymer and copolymer architectures, is actually perceived as a most convincing demonstration of the said association. In reality, *designing* one such catalyst from scratch is still a dream, and behind all reported discoveries is the classical mix of hard work and serendipity.

As a demonstration, we wish to discuss here the paradigmatic case of propene polymerization promoted by octahedral C₂-symmetric column 4 catalysts with phenoxy-imine³ (Chart 1, **I**) or phenoxy-amine⁴ (Chart 1, **II**) ligands. On inspection, the local coordination environment of the metal center looks closely similar in the two systems. In accordance with the expectation of all those skilled in the art, catalysts of type **II** (Mt = Zr) afford *isotactic* polypropylene via highly 1,2 (*primary*) monomer insertion.^{4,5} Quite unpredictably, catalysts of type **I** (Mt = Ti) turned out instead to produce *syndiotactic* polypropylene with a predominantly 2,1 (*secondary*) insertion mode.^{3,6–8}

In the following, we offer a theoretical explanation for the opposite *regioselectivities* of the two systems, which stem from an extremely subtle interplay of electronic and steric effects. The origin of the different *stereoselectivities*, already addressed elsewhere,^{9,10} is beyond the scope of this paper.

Quantum mechanics/molecular mechanics methods^{11,12} (QM/MM, see Supporting Information) were used to calculate, for suitable models of catalytic species (vide infra), the energy difference between the transition states for 2,1 and 1,2 propene insertion ($\Delta E_{\text{regio}}^{\ddagger}$) into the Mt–Me, Mt–*i*Bu, and Mt–*i*Pr bonds to simulate chain initiation and chain propagation at a primary and a secondary growing chain, respectively. The results are summarized in Table 1.

Let us consider **I**-Ti first. According to the calculations, propene insertion into **I**-Ti–Me is predominantly 1,2 ($\Delta E_{\text{regio}}^{\ddagger} = 1.0$ kcal/mol), but this preference almost vanishes for **I**-Ti–*i*Bu ($\Delta E_{\text{regio}}^{\ddagger} = 0.3$ kcal/mol). Importantly, insertion into **I**-Ti–*i*Pr is instead remarkably regioselective in favor of the 2,1 mode ($\Delta E_{\text{regio}}^{\ddagger} = -2.0$ kcal/mol); this means that, after a first 2,1 insertion, secondary propagation tends to be maintained. All this agrees nicely with the experiment.^{3,6–8}

The QM/MM results for **II**-Zr are also in line with the experimental finding. In fact, all $\Delta E_{\text{regio}}^{\ddagger}$ values reported in Table 1 are positive; i.e., 1,2 insertion is always favored, also at **II**-Zr–*i*Pr ($\Delta E_{\text{regio}}^{\ddagger} = 1.4$ kcal/mol).

According to the calculations, the qualitative behavior of **I**-Mt and **II**-Mt is *not* strongly dependent on the choice of metal.

Chart 1

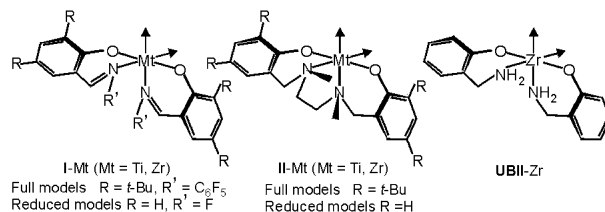


Table 1. Energy Differences (kcal/mol) between the Transition States for 2,1 and 1,2 Propene Insertion ($\Delta E_{\text{regio}}^{\ddagger}$) for Full and “Reduced” Models of **I**-Mt and **II**-Mt, and for **UBII**-Zr (Chart 1)

model	alkyl	$\Delta E_{\text{regio}}^{\ddagger}$	
		full model	reduced model
I -Ti	methyl	1.0	2.2
I -Ti	isobutyl	0.3	0.1
I -Ti	isopropyl	-2.0	-3.0
I -Zr	isobutyl	0.9	1.0
I -Zr	isopropyl	-1.4	-1.3
II -Zr	methyl	5.5	5.9
II -Zr	isobutyl	3.6	4.0
II -Zr	isopropyl	1.4	1.1
II -Ti	isobutyl	4.4	4.3
II -Ti	isopropyl	2.4	1.7
UBII -Zr	isobutyl		2.0
UBII -Zr	isopropyl		0.1

Therefore, these dramatically different regioselectivities must be traced to electronic and/or steric effects related to the ancillary ligand(s). To identify and quantify such effects *separately*, we first repeated our calculations on “reduced” models of **I**-Mt and **II**-Mt (Chart 1). Despite small changes in the values of $\Delta E_{\text{regio}}^{\ddagger}$, the data in the last two columns of Table 1 clearly indicate that the predicted regioselectivities of corresponding full and reduced models are fairly similar for both **I**-Ti and **II**-Zr. Therefore, the bulky *t*Bu groups and the C₆F₅ rings are *not* relevant for the regiochemistry.

As a second step, we explored the role of the *steric* interactions between the methyl group of propene and the catalyst ligand framework for the reduced models. To this end, we performed QM/MM calculations, in which the monomer was represented as ethene at the QM level, whereas the methyl group was introduced at the MM level. Independently of the metal, for propene insertion into **I**-Mt–*i*Bu and **I**-Mt–*i*Pr bonds, we calculated $\Delta E_{\text{regio}}^{\ddagger}$ values close to 0.5 and -1.5 kcal/mol, respectively; corresponding values for **II**-Mt–*i*Bu and **II**-Mt–*i*Pr are ca. 1.5 and -0.5 kcal/mol. Not surprisingly, this indicates that sterics favors 1,2 insertion when the growing chain is primary; 2,1 insertion, instead, is preferred when the growing chain is secondary, because it does not require the formation of a sterically demanding head-to-head enchainment.¹³

Within this general statement, from the above $\Delta E_{\text{regio}}^{\ddagger}$ values it appears that, still from a steric viewpoint, systems **II**-Mt are slightly

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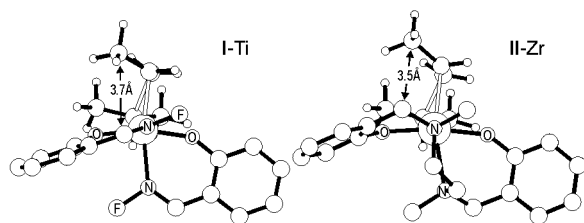


Figure 1. Rear view of the transition states for secondary propene insertion into the Mt–*i*Pr bond of **I-Ti** and **II-Zr**. Short distances between the propene methyl group and ligand C atoms are indicated.

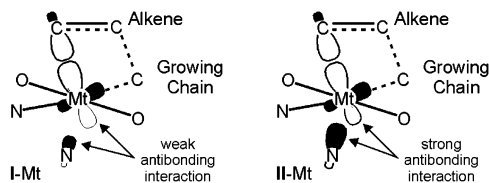


Figure 2. Schematic representation of the most relevant part of the MO corresponding to the incipient Mt–C bond in systems **I-Mt** and **II-Mt**.

more 1,2-orientating than **I-Mt**. This can be traced to repulsion between the methyl of a 2,1-inserting propene molecule and the CH₂ group bound to the amine N atom of ligand **II**, protruding toward the incoming monomer due to the sp³ N hybridization (Figure 1, right). Instead, for **I-Mt**, the sp² hybridization of the N atoms alleviates steric crowding (Figure 1, left). However, we note that even removing the bridge and replacing H for CH₃ on the N in **II-Zr** (ending up with **UBII-Zr**, Chart 1) did not result in a dramatic change of $\Delta E_{\text{regio}}^{\ddagger}$. Therefore, we conclude that sterics alone is *not enough* to justify the opposite regioselectivities of **I-Mt** and **II-Mt**.

An analysis of the molecular orbitals (MOs) at the transition states for propene insertion revealed that the MO corresponding to the incipient Mt–C bond is destabilized by an antibonding interaction with the MO corresponding to the lone pair of the N atom opposite to it (Figure 2). This trans influence is stronger for **II-Mt** systems, because the lone-pair MO of the *amine* N is roughly 3 eV higher in energy than the corresponding orbital of the *imine* N of **I-Mt** systems.¹⁴ Of course, when propene insertion is 2,1, the donating effect of the methyl group on the electron density of the incipient Mt–C bond is larger, which results, in turn, in a stronger antibonding interaction.

To quantify this effect, we evaluated the Mt–(primary alkyl) and Mt–(secondary alkyl) fragmentation energies in neutral dialkyl systems of the type **L-Mt(Me)(*n*Pr)** and **L-Mt(Me)(*i*Pr)** (**L = I, II**; Mt = Ti, Zr). In particular, we rigidly fragmented the optimized structure of the neutral dialkyl systems as indicated in eq 1.



The Mt⁺/propyl[−] interaction energies (IEs), scaled to the stronger **I-Ti(Me)⁺/*i*Pr[−]** interaction, are reported in Table 2. For each system, the difference in Mt⁺/*i*Pr[−] and Mt⁺/*n*Pr[−] interactions ($\Delta E_{nPr-iPr}$) is also reported. The data clearly indicate that all **II-Mt⁺/propyl[−]** interactions are roughly 10 kcal/mol weaker than **I-Mt⁺/propyl[−]** ones, due to the larger trans influence of the *amine* N (compared with the *imine* N). Moreover, the smaller $\Delta E_{iPr-nPr}$ values calculated for **II-Mt** indicate that the destabilization is larger for the more electron-donating *i*Pr group than for the *n*Pr group, which points to an electronic preference of **II-Mt** for 1,2 propene insertion.

In conclusion, the opposite regioselectivities of **I-Ti** and **II-Zr** can be traced to a complicated concourse of synergic steric and electronic effects. The key element is the different nature of the

Table 2. Interaction Energies (IE, kcal/mol) between the **L-Mt(Me)⁺** and Propyl Fragments^a

species	IE _{<i>i</i>Pr}	IE _{<i>n</i>Pr}	$\Delta E_{nPr-iPr}$
I-Ti	0	−3.0	−3.0
I-Zr	−1.8	−4.0	−2.2
II-Ti	−11.0	−12.1	−1.1
II-Zr	−11.4	−11.8	−0.4

^a Values are scaled to the stronger **I-Ti(Me)⁺/*i*Pr[−]** interaction. For each species, $\Delta E_{nPr-iPr} = IE_{nPr} - IE_{iPr}$ is also reported. Negative IE values mean weaker interactions.

ligand N atoms in the two systems. The *imine* N's of **I-Ti** favor 2,1 propene insertion because their sp² hybridization reduces the steric interactions of the inserting monomer with the ligand framework (Figure 1) and results in a comparatively mild antibonding interaction with the incipient Mt–C bond (Figure 2 and Table 2). Conversely, the *amine* N's of **II-Zr** favor 1,2 insertion because their sp³ hybridization introduces steric congestion with an incoming 2,1 propene and determines a strong antibonding interaction with the incipient Mt–C bond, particularly when C is methyl-substituted.

Thus, the roles played by the nature of the metal, and by the steric and electronic properties of the ligand, in determining the regiochemistry of propene insertion at octahedral catalysts have been sorted out. The $\Delta E_{\text{regio}}^{\ddagger}$ values in Table 1 show that suitable combinations of these effects result in regiochemistries gradually varying from clearly primary (1,2) to clearly secondary (2,1). We believe this may help to design octahedral propene polymerization catalysts with tailored regioselectivity.

Acknowledgment. We thank Dr. P. H. M. Budzelaar (University of Nijmegen) and Dr. H. Jacobsen (KemKom) for useful discussions, and the CIMCF of the University of Napoli Federico II for technical assistance. This work was supported by the MURST of Italy (Grants PRIN 2002 and FISR). L.C. thanks Prof. T. K. Woo and the SHARCNET project (University of Western Ontario) for generous access to computer facilities.

Supporting Information Available: Details on the calculation methods, test calculations, Cartesian coordinates, and energies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- For example, we calculated the lone-pair MO of N(CH₃)₃ to be 2.7 eV higher in energy than the lone-pair MO of CH₂=NF.

JA029604O