1028 *Organometallics* **2008,** *27,* 1028–1029

Electronic Effects on Regioselectivity in Styrene Polyinsertion Promoted by Group 4 Catalysts

Andrea Correa, Nunzia Galdi, Lorella Izzo, Luigi Cavallo, and Leone Oliva*

Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, I-84084 Fisciano (SA), Italy

Received October 17, 2007

Summary: The effect of electron density at the incoming metal–carbon bond on the regiochemistry of styrene insertion into the zirconium−carbon bond is evidenced through experimental results and computational studies.

The regiochemistry of styrene insertion into the metal–carbon bond is a complex issue, with several experimental data showing different behaviors, depending on the specific catalytic system investigated. The heterogeneous Ziegler–Natta catalysts, promoting isospecific styrene polymerization, insert the monomer in a primary fashion: that is, with formation of $TiCH_2CH(Ph)R$ bonds.[1] On the other hand, the opposite regiochemistry has been generally observed with a variety of homogeneous systems. For example, with both tetrabenzyltitanium and tetrabenzylzirconium activated by methylalumoxane (MAO) Zambelli et al.[2] evidenced secondary insertion in syndioselective styrene polymerization, both in the initiation and in the chain growth steps. Still secondary is styrene insertion in the dimerization catalyzed by bis(2,4,7-trimethylindenyl)yttrium hydride[3] and by a ruthenium complex,[4] whereas Marks et al. reported primary insertion in competition with the secondary insertion in the presence of a bimetallic titanium-based system.[5] Finally, with MAO-activated *ansa*-zirconocenes insertion is prevailingly secondary,[6] but the regiochemistry can be inverted by tailoring the encumbrance of the coordinative framework.[7] This latter evidence seems in accordance with the regiochemistry of propene insertion with group 4 metallocenes, which is clearly dominated by steric effects.[8]

In order to investigate the role of electronic effects on the regioselectivity of styrene insertion with group 4 catalysts, we devised an experiment where the ability of the electronic factors to affect the regiochemistry is highlighted. Specifically, we evaluated the regioselectivity of insertion of para-substituted styrenes into the Zr−alkyl bond of the prototype *rac*-bis(indenyl)zirconocene. We selected this catalyst because it allows a clear-cut separation between steric and electronic factors (vide infra). Using styrene as reference (Hammett constant $\sigma = 0$), we choose four para-susbtituted styrenes: two with an electron-donating group (NH_2, $\sigma = -0.66$; Me, $\sigma = -0.17$) and two with an electron-withdrawing group (Cl, $\sigma = 0.21$; NO_2, $\sigma = 0.78$). Since the substituent is in the para position, i.e. far away from the ligand and the growing chain, steric effects can be considered identical among the various systems. Thus, any difference in regioselectivity can, without doubt, be ascribed to electronic effects only.[9]

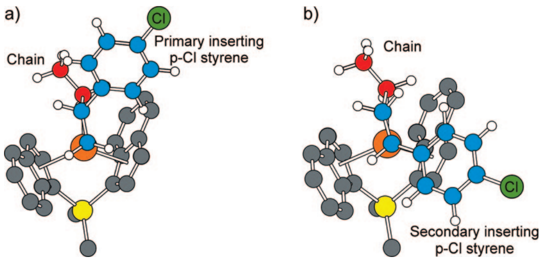


Figure 1. Transition states for primary (a) and secondary (b) insertion of *p*-Cl-styrene into the $Zr{-}C_2H_5$ bond of the *rac*-$Me_2Si(Ind)_2Zr$-based zirconocene.

Using a standard DFT approach,[10] we calculated the shift in regioselectivity, $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$,[11] of four substituted styrenes relative to styrene. Negative (positive) values of $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ imply that regioselectivity is shifted toward secondary (primary) monomer insertion. The transition states for primary and secondary *p*-Cl-styrene insertion into the $Zr{-}C_2H_5$ bond, to simulate monomer insertion into a Zr−(primary chain) bond of a *rac*-$Me_2Si(Ind)_2Zr$-based catalyst, are reported in Figure 1. Geometrical inspection clearly indicates that in both transition states the *p*-Cl substituent is located far away from both the bis(indenyl) ligand and the growing chain (shortest distance > 5 Å). This confirms that the selected systems allow isolating unequivocally electronic effects. The theoretical $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ values of the monomers that can be tested experimentally, *p*-Cl- and *p*-Me-styrenes, are negative and positive, respectively (see Table 1), which indicates that the regioselectivity of *p*-Cl and *p*-Me styrenes relative to styrene should be shifted toward secondary and primary insertion, respectively.

---

* To whom correspondence should be addressed. E-mail: loliva@unisa.it.

(1) Ammendola, P; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307–310.

(2) (a) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277–279. (b) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035–2037.

(3) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284–286.

(4) Kondo, T.; Takagi, D.; Tsujita, H.; Ura, Y.; Wada, K.; Mitsudo, T. *Angew. Chem.* **2007**, *46*, 5958–5961.

(5) Guo, N.; Li, L.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 6542–6543.

(6) (a) Oliva, L.; Caporaso, L.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1995**, *28*, 4665–4667. (b) Caporaso, L.; Izzo, L.; Oliva, L. *Macromolecules* **1999**, *32*, 7329–7331.

(7) Izzo, L.; Napoli, M. G.; Oliva, L. *Macromolecules* **2003**, *36*, 9340–9345.

(8) (a) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394–4403. (b) Correa, A.; Talarico, G.; Cavallo, L. *J. Organomet. Chem.* **2007**, *692* (21), 4519–4527.

(9) A different strategy could have been modifying the electronic properties of the ligand and checking the effect on styrene insertion. However, even small structural changes in the ligand could raise the doubt that the effects on regiochemistry could be steric in nature.

(10) DFT calculations were performed at the B3LYP level. The SVP basis set was used for H, C, Si, and Cl, while the ECP/SDD basis set was used for Zr. Full details can be found in the Supporting Information.

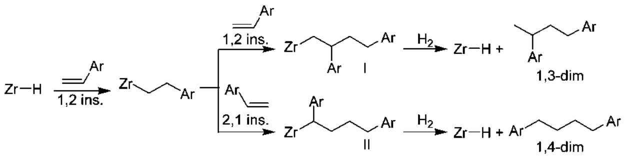
(11) In the framework of the Curtin-Hammett principle, see: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83, $\delta\Delta\Delta G^{\ddagger}_{\text{regio}} = (\Delta\Delta G^{\ddagger}_{\text{regio}})_{p\text{-X}} - (\Delta\Delta G^{\ddagger}_{\text{regio}})_{\text{styrene}}$, where $\Delta\Delta G^{\ddagger}_{\text{regio}}$ is the energy difference between the transition states for secondary and primary monomer insertion, respectively.

10.1021/om701039e CCC: $40.75

Table 1. Ratio between the Regioregular 1,3- and Regioirregular 1,4-Hydrodimers, [1,3-dim]/[1,4-dim], and the Corresponding Experimental and Theoretical $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ Values, in kcal/mol

			$\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$	
monomer	σ	[1,3-dim]/[1,4-dim]	exptl	theor
p-NO_2-styrene	0.78			−1.63
p-Cl-styrene	0.21	0.32	−0.14	−0.71
styrene	0	0.40	0	0
p-Me-styrene	−0.17	0.55	0.21	0.28
p-NH_2-styrene	−0.66			2.00

Scheme 1



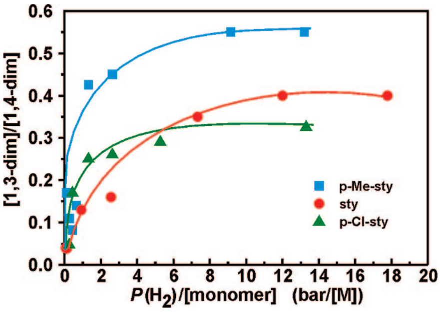


Figure 2. Plot of [1,3-dim]/[1,4-dim] ratio versus H_2 feed composition.

This clearly suggests an important role of electronic effects on the regioselectivity of styrene insertion, although the small variation in $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ values predicted for *p*-Cl- and *p*-Me-styrenes could cast doubts about their reliability. Strong support comes from calculations on the *p*-NO_2- and *p*-NH_2-substituted styrenes, which are at the extreme of the Hammett scale. In fact, the $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ values reported in Table 1 for these two systems, which cannot be tested experimentally, strongly deviate in favor of secondary and primary insertion, respectively.

In order to experimentally evaluate the effect of the substituents, we took advantage of hydrooligomerization techniques developed for the same systems.[12] Specifically, we estimated the regioselectivity of *p*-Me- and *p*-Cl-styrene relative to styrene as the ratio between the regioregular 1,3-hydrodimer (1,3-dim) and the regioirregular 1,4-hydrodimer (1,4-dim) obtained with the *rac*-$C_2H_4(H_4\text{-Ind})_2ZrCl_2$-based catalyst.[13]

In accord with Scheme 1 and previous considerations,[12] we can state that the regioregular 1,3-hydrodimer is formed by monomer primary insertion into the metal−hydride bond followed by further primary insertion into the metal–carbon bond. In contrast, the regioirregular 1,4-hydrodimer still arises from primary insertion into the metal−hydride bond but is followed by secondary insertion into the metal–carbon bond. As a consequence, the ratio between the amounts of the hydrodimers, [1,3-dim]/[1,4-dim], represents the relative reactivity of primary versus secondary insertion, provided the sole fate of intermediates I and II is hydrogenolysis.

On this basis we performed for each para-substituted styrene a series of hydrooligomerizations at increasing H_2/monomer ratios. In Figure 2 the experimental [1,3-dim]/[1,4-dim] ratio versus the feed composition is reported. The extrapolated values are reported in Table 1 together with the experimental $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ values of activation obtained by assuming that the hydrooligomer ratio corresponds to the ratio of the kinetic constants for the primary and secondary insertion into the same Zr−C bond.

Experiments confirm that para electron-donating groups shift monomer insertion toward primary insertion, whereas para electron-withdrawing groups shift monomer insertion toward secondary insertion. It is worth noting that the effect is rather strong, since the $\delta\Delta\Delta G^{\ddagger}_{\text{regio}}$ values we reported are due to a substituent far away from the metal. Considering the consistency between the whole mechanistic scenario proposed and the theoretical and experimental results, we believe our conclusions are useful to enlighten the regiochemistry of styrene insertion into the M−alkyl bond of group 4 complexes.

The main message conveyed by this study is that increasing the electron density at the incoming metal–carbon bond increases the tendency toward primary insertion. It is tempting to suggest that changing the ligand skeleton and/or the metal could have a far greater effect. Work is in progress to test this idea, by tuning the electronic properties of the metallic center.

Acknowledgment. This work was supported by Basell Polyolefins and Cineca Italy (Grant INSTM).

Supporting Information Available: Text and tables giving details of the calculation methods and experimental procedures and Cartesian coordinates and energies of all the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701039E

---

(12) Galdi, N.; Della Monica, C.; Spinella, A.; Oliva, L. *J. Mol. Catal. A: Chem.* **2006**, *243*, 106.

(13) Hydrooligomerizations were carried out at 50 °C in a 250 mL steel autoclave or in a 100 mL glass flask charged, under vacuum, with the monomer, MAO, *rac*-$C_2H_4(H_4Ind)ZrCl_2$ ((mol of Al)/(mol of Zr) = 1000), and toluene when necessary. Then the hydrogen was fed at the desired pressure (1, 5, 8, or 40 atm). After 9 h the reaction mixture was quenched into acidified ethanol and the hydrodimers were recovered, after removal of the catalytic ashes, by distillation under reduced pressure.