Supporting Information for

Mechanistic Details on Ethylene Polymerization Reaction: Using Methallyl Nickel(II) Catalysts

Daniela E. Ortega, ^a Diego Cortés-Arriagada^b and Alejandro Toro-Labbé^{*a}

^a Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-22, Chile. E-mail: atola@uc.cl
^b Programa Institucional de Fomento a la Investigación, Desarrollo e Innovación, Universidad Tecnológica Metropolitana, Ignacio Valdivieso 2409, P.O. Box 8940577, San Joaquín, Santiago, Chile.

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I. Fragment Charge Analysis

It has been shown that the REF is a very useful tool to identify electronic activity along the reaction coordinate. In this context it is possible to complement some characteristics observed in the REF with respect to their nature. it must also affect atomic and group charges as it did with bond orders and dipole moments.

Charges of molecular fragments according to Figure S1, results from the natural population analysis (NPA) are shown in Figure S2. Looking first at the trends in the Ni-complex, it presents a sharp decrease in the positive charge from ξ_R to ξ_1 , which is followed by an increase from ξ_1 to ξ_P . The negative charge on ethylene exhibits the same trend for both reactions. However, as the σ and π components have an opposite effect upon the charges. Hence, from a qualitative point of view, we can confirm the above results where the σ donation seems to be stronger at the beginning of the reaction, increasing and decreasing the ethylene and Ni-complex charge at the reactant region, being at this zone of the reaction where this phenomena take place. Within the transition state region, once that the π -bond of the ethylene is weaken *via* a stronger σ -donation, the hybridization of the ethylene is reflect of a large decrease of the net charge until reach the product. This trend is caused by fact that the σ -bond of the ethylene is reached by an operative π -back donation process at this point of the reaction; while σ -donation becomes stronger only when the π -bond of the ethylene exists. In this context, π -back donation in terms of the charge shifts shows a higher split in **R2** than **R1** between Ni-complex and ethylene in the product (see Figure S2; $\xi_{\rm P}$). This can be explained from purely electrostatic effect of the ligand functionalization by $B(C_6F_5)_3$. The electronegative nature of fluorine atoms of the $B(C_6F_5)_3$ structure on the Nicenter has a greater impact on **R1**, which could binds a stronger π -back bonding effect product of major electrostatic interactions. Therefore, we could assume that π -back donation to be associated to purely electrostatic effect of the B(C₆F₅)₃ from the functionalization on the catalyst (π -donation; **C1** > **C2**) and infer from high steric effect of the B(C₆F₅)₃ on the catalyst how weak the σ -bonding must be (σ -donation; **C1** < **C2**).



Figure S1. Fragmentation of the supermolecule in terms of ethylene (fragment 1) and Nicomplex (fragment 2) for ethylene polymerization process (I_{nit} , P_{rop} and T_{erm}) in the complexes C1 (black) and C2 (red).



Figure S2. Fragment charges for ethylene (orange) and Ni-complex (magenta) along the reaction coordinate for **R1** and **R2** reactions.

II. Fragment Charge Transfer Analysis

The σ -donation and π -back donation processes were also analyzed on the basis of nucleophilic (N_{nucl}) and electrophilic (N_{elec}) channels (Figure S3) developed by Orozco-Valencia and co-workers (*Journal of molecular modeling* **2017**, *23*, 207). This tool has been defined using directional chemical potentials ($\mu^- \approx \varepsilon_H$ and $\mu^+ \approx \varepsilon_L$) and the hardness among the ethylene and Ni-complex species as measure of net charge process. In fact, we have found a good correlation between our previous results with respect to the charge transfer process and the obtained by this definition, confirming that the σ -donation is initially stronger (Figure S3; N_{elec}>N_{nucl}) and the Ni-complex behaves like an electrophic at the *R* and *TS* structures in front of the ethylene, which implies that the ethylene donate

charge to the Ni-complex. While, the π -donation becomes stronger at the end of the reaction (Figure S3; N_{elec} < N_{nucl}), and the Ni-complex behaves like an nucleophic at the P structure in front of the ethylene, being the Ni-complex the donor species.



Figure S3. Net charge transfer process on catalyst (a) C1 and (b) C2 for the ethylene polymerization process (Init, Prop and Term). Nnucl (square) and Nelec (triangle) denotes the electrophilic nucleophilic the With and channel for the catalyst. $N_{nucl}^{Ni-complex} = \frac{\mu_{ethylene} - \mu_{Ni-complex}}{2(\eta_{Ni-complex} + \eta_{ethylene})}$ – N^{ethylene} $\frac{\mu_{ethylene}^{+} - \mu_{Ni-complex}^{-}}{2(\eta_{Ni-complex} + \eta_{ethylene})}$ $N^{Ni-complex}_{elec} =$ $=-N^{ethylene}_{nucl}$ $N^{Ni - complex}_{nucl}$ and the (N_{nucl}) is

represented in absolute values on the graphics.

On the other hand, it is worth highlighting some interesting differences along the polymerization process between C1 (Figure S3a) and C2 (Figure S3b): (a) at the beginning of the Init step (Figure S3; Init-R structure), C1 present a larger value of N_{elec} (greater electrophilicity) than C2, which confirms that the *ortho*-functionalization caused by larger steric effect of B(C₆F₅)₃ is responsible of the slightly higher energy barrier. (b) At the end

of the **Prop** step (Figure S3; **Prop**-P structure), **C2** behaves highly as nucleophilic and electrophilic ($N_{elec} \sim N_{elec}$), we could be assumed that its reactive duality allows it to propagate as well as to finish the growth of the chain, confirming why this complex is able to form chains of lower molecular weight. (c) At the end of the **Term** step (Figure S3; **Term**-P structure), **C1** present a larger value of Nnucl (greater nucleophilicity) than **C2**, associated to purely electrostatic effect of the B(C₆F₅)₃ in *ortho*-position.