

# Supporting Information File

## Insight into Group 4 Metallocenium-Mediated Olefin Polymerization Mechanisms using a Metadynamics Approach

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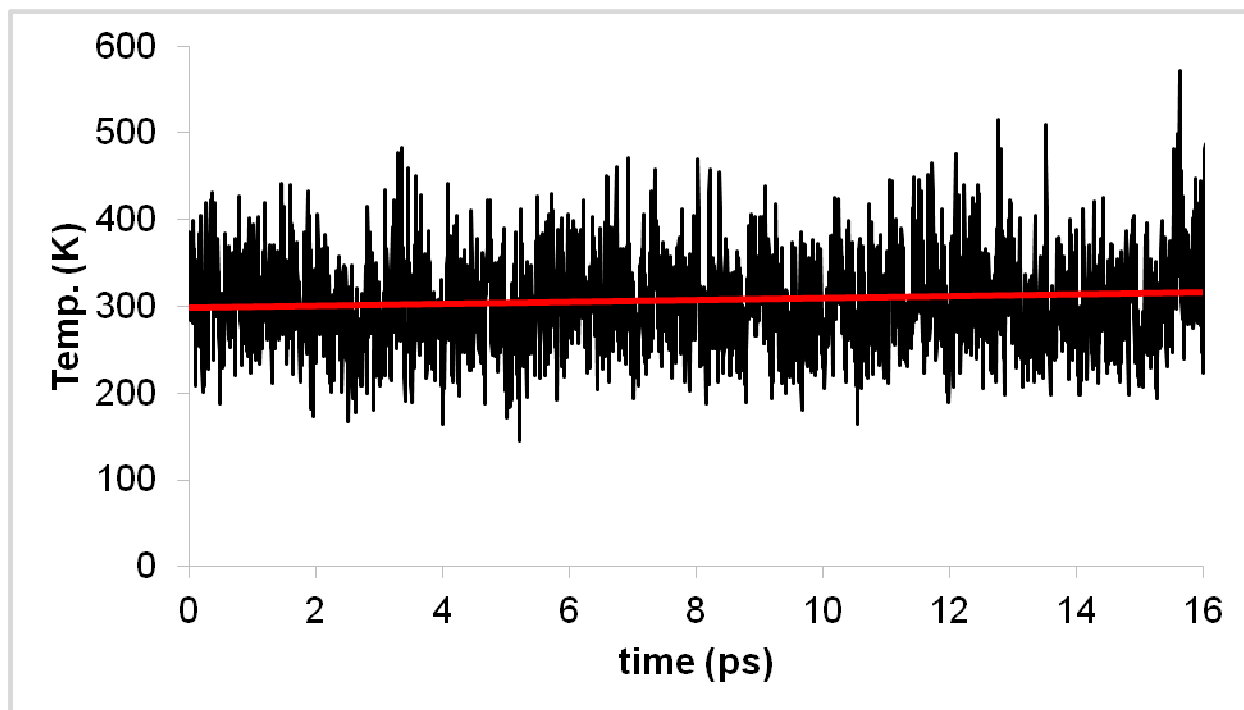


Figure S1. QM temperature of the system during simulation. In black is reported the temperature fluctuations and in red the temperature running average.

Table S1. Computed Gibbs free energies of species on the ethylene insertion pathway at the  $(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\text{CH}_3)_2^+$  cation computed by the static and metadynamic approaches (kcal/mol) with different approximations.

	<i>Static</i>			<i>MD</i> <sup>a</sup>
	B3-LYP	PBE	PBE-vdW <sup>b</sup>	
$\pi$ -complex	0.0	0.0	0.0	0.0
Insertion TS	12.6	7.9	7.6	8.6
Insertion product	-1.0	-5.0	-5.4	-3.2

<sup>a</sup> In the MD approach the vdW contribution is enclosed. <sup>b</sup> vdW contribution shows slightly effects on the relative energies

Cartesian coordinates (Å) of the optimized structures involved in the ethylene insertion step at (Cp)Zr(Me)<sub>2</sub><sup>+</sup> catalyst obtained by static calculations.

Ethylene π complex at (Cp)Zr(Me)<sub>2</sub><sup>+</sup>

C	-1.309876000	1.187754000	1.157798000
C	-0.854135000	1.893739000	-0.000006000
C	-2.045515000	0.053091000	-0.720930000
C	-1.309878000	1.187745000	-1.157805000
C	-2.045513000	0.053096000	0.720933000
H	-1.118285000	1.462010000	2.196087000
H	-0.316450000	2.841494000	-0.000011000
H	-2.533556000	-0.678829000	-1.363438000
H	-1.118289000	1.461993000	-2.196096000
H	-2.533553000	-0.678818000	1.363448000
Zr	0.284156000	-0.393363000	0.000001000
C	0.147572000	-1.747260000	-1.714538000
H	-0.075027000	-1.325565000	-2.707705000
H	-0.566324000	-2.570298000	-1.520439000
H	1.168907000	-2.199348000	-1.736382000
C	0.147581000	-1.747238000	1.714558000
H	-0.075012000	-1.325530000	2.707721000
H	-0.566317000	-2.570279000	1.520474000
H	1.168916000	-2.199328000	1.736403000
H	2.967090000	0.013293000	-0.939772000
C	2.669443000	0.502316000	-0.000009000
C	2.153782000	1.763770000	-0.000013000
H	2.967094000	0.013300000	0.939757000
H	1.971903000	2.304178000	-0.934795000
H	1.971907000	2.304185000	0.934766000

Ethylene Insertion Transition State

C	1.154293000	-1.749727000	-0.160975000
C	1.625862000	-0.841475000	-1.160268000
C	2.083510000	0.077419000	0.904130000
C	2.225077000	0.279010000	-0.498824000
C	1.425811000	-1.182643000	1.115500000
H	0.651469000	-2.700552000	-0.344080000
H	1.569177000	-0.992454000	-2.239900000
H	2.424047000	0.760750000	1.684544000
H	2.687072000	1.140837000	-0.979125000
H	1.192358000	-1.631277000	2.081919000
Zr	-0.237794000	0.349623000	0.029959000
C	0.000162000	2.465333000	-0.492521000

H	0.269199000	2.556979000	-1.565248000
H	0.723763000	3.071922000	0.077601000
H	-1.008504000	2.917862000	-0.355733000
C	-1.677509000	0.085421000	1.692360000
H	-0.697222000	0.323258000	2.223573000
H	-2.298263000	1.002728000	1.694179000
H	-2.153655000	-0.693583000	2.299155000
H	-3.394098000	-0.375681000	-0.054304000
C	-2.534129000	-1.006190000	-0.296443000
C	-1.766287000	-0.773596000	-1.433385000
H	-2.471909000	-1.962708000	0.229186000
H	-2.034326000	0.058647000	-2.103966000
H	-1.168094000	-1.582959000	-1.863592000

Kinetic product of ethylene insertion into (Cp)Zr(Me)<sub>2</sub><sup>+</sup>

C	-1.611412000	-0.666021000	1.235341000
C	-2.270093000	0.216877000	0.319003000
C	-1.316858000	-1.510277000	-0.892924000
C	-2.079020000	-0.301925000	-0.996735000
C	-1.036365000	-1.735882000	0.487287000
H	-1.555337000	-0.543927000	2.317239000
H	-2.821719000	1.118916000	0.578832000
H	-1.017132000	-2.152827000	-1.723433000
H	-2.447858000	0.146806000	-1.920824000
H	-0.455152000	-2.561424000	0.899354000
Zr	0.157556000	0.373046000	-0.162137000
C	-0.342366000	2.488798000	0.106881000
H	-1.165123000	2.919198000	-0.486107000
H	0.603947000	3.013858000	-0.166983000
H	-0.539244000	2.709428000	1.174558000
C	2.402488000	-0.290574000	-1.135112000
H	1.522758000	-0.654645000	-1.743979000
H	2.533090000	0.808596000	-1.258153000
H	3.235041000	-0.738124000	-1.699802000
H	3.531404000	-0.557213000	0.653362000
C	2.492371000	-0.787488000	0.361878000
C	1.531035000	-0.165524000	1.422787000
H	2.380672000	-1.882561000	0.350695000
H	1.922378000	0.805119000	1.794992000
H	1.351339000	-0.840939000	2.265298000