

Supporting Information

Ancillary Ligand Effects on α -olefin Polymerization Catalyzed by Zirconium Metallocene: A Computational Study

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Table S1. Computed energy profiles for **Cat.1** mediated coordination insertion of **m** in the chain initiation and chain propagation stages. Free energies are relative to isolated reactants. The most favorable pathways are in green.

	First insertion				Second insertion			
Mode	Coor.	TS	Pro.	ΔG^\ddagger	Coor.	TS	Pro.	ΔG^\ddagger
1,2- <i>re</i>	-3.4	12.3	-6.8	15.7	-8.5	3.1	-16.2	11.6
1,2- <i>si</i>	-0.7	11.4	-8.0	12.1	2.8	5.8	-19.3	13.8
2,1- <i>re</i>	-1.4	20.8	4.8	22.2	/			
2,1- <i>si</i>	-2.2	16.9	-1.3	19.1	/			
	Third insertion				Fourth insertion			
Mode	Coor.	TS	Pro.	ΔG^\ddagger	Coor.	TS	Pro.	ΔG^\ddagger
1,2- <i>re</i>	-8.3	-4.9	-27.0	11.3	-16.5	-15.1	-35.0	11.9
1,2- <i>si</i>	-6.8	-4.4	-25.1	11.8	-12.0	-8.3	-31.4	18.8

Table S2. Computed energy profiles for **Cat.2** mediated coordination insertion of **m** in the chain initiation and chain propagation stages. Free energies are relative to isolated reactants. The most favorable pathways are in green.

	First insertion				Second insertion			
Mode	Coor.	TS	Pro.	ΔG^\ddagger	Coor.	TS	Pro.	ΔG^\ddagger
1,2- <i>re</i>	-4.8	10.9	-7.0	14.4	-10.7	1.4	-14.8	12.1
1,2- <i>si</i>	-3.2	9.7	-7.1	12.9	-9.6	4.2	-19.0	13.8
2,1- <i>re</i>	-4.4	17.5	-0.8	21.9	/			
2,1- <i>si</i>	-4.3	14.7	-6.0	18.9	/			
	Third insertion				Fourth insertion			
Mode	Coor.	TS	Pro.	ΔG^\ddagger	Coor.	TS	Pro.	ΔG^\ddagger
1,2- <i>re</i>	-18.4	-8.5	-26.1	9.9	-22.8	-15.9	-37.2	10.5
1,2- <i>si</i>	-17.9	-6.5	-27.2	12.0	-22.7	-10.5	-31.0	15.9

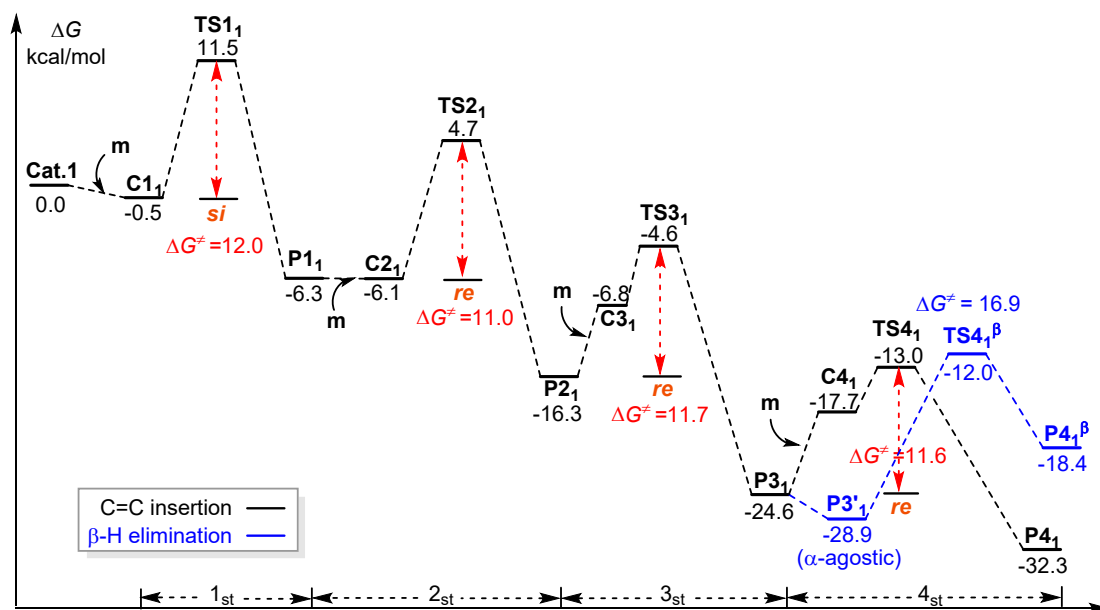


Figure S1. Computed energy profiles (M06(SMD)/6-311G** \cap SDD//B3PW91+D3/6-31-G** \cap SDD) for **Cat.1** mediated chain initiation and chain propagation of **m**. The C=C insertion and β -H elimination pathways are indicated in black and blue, respectively.

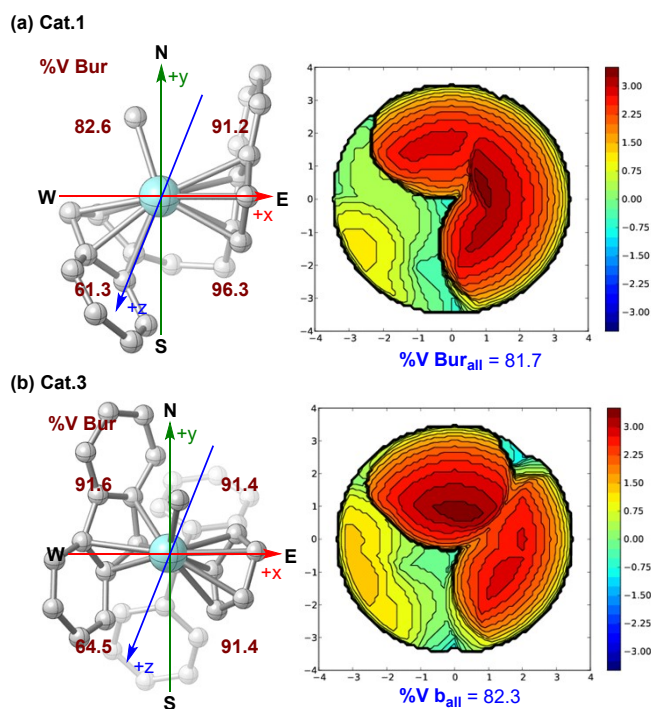


Figure S2. Topographical steric maps of catalysts **1** and **2**.