Supporting Information

Separating electronic from steric effects in ethene/α-olefin copolymerization: A case study on octahedral [ONNO] Zr-catalysts

Francesco Zaccaria[1,2], Roberta Cipullo[1], Andrea Correa[1], Peter H. M. Budzelaar[1], Vincenzo Busico[1] and Christian Ehm[1,*]

[1] Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia, 80126 Napoli (Italy)

[2] present address: Dipartimento di Chimica, Biologia e Biotecnologie and CIRCC, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia (Italy)

[*] Correspondence: christian.ehm@unina.it

- **Polymerization results**

Table S1. Experimental results for catalysts **1** in ethene/butene (*E/B*) copolymerization.

Entry	Catalyst	$p(E)$, bar	n(Zr), µmol	X_i[a]	X_f[a]	R_p[b]	$[B]_{cop}$,[c] mol%	$10^{-2} \times P_n$[d]	r_E	r_B	$r_E r_B$
1	MeMe	1.1	38	0.0460	0.0464	0.5	24	1.0	61(6)	0.011(1)	0.7(1)
2		0.55	40	0.0225	0.0241	1.0	39	0.91	59(6)	0.013(1)	0.7(1)
3	MeCl	1.1	37	0.0472	0.0526	7	32	0.53	42(4)	0.021(2)	0.9(2)
4		0.55	38	0.0238	0.0278	19	53	0.50	34(3)	0.028(3)	1.0(2)
5	ClMe	1.1	6.0	0.0543	0.0584	31	37	0.24	33(3)	0.037(3)	1.2(2)
6		0.55	5.7	0.0200	0.0220	15	59	0.27	33(3)	0.030(3)	1.0(2)
7	ClCl	1.1	4.1	0.0552	0.0610	360	43	0.22	22(2)	0.041(4)	0.9(2)
8		0.55	3.9	0.0233	0.0295	281	71	0.26	22(2)	0.068(7)	1.5(3)

In toluene (150mL); 25 °C; p(B) = 1.1 bar; cocatalyst = MAO/TBP ([Al] = 5.4 × 10^{-2} M). E = ethene; B = butene. [a] Initial (*i*) and final (*f*) comonomer feeding ratio ([E]/[B], see also Materials and Methods section); [b] Productivity in kg(copolymer) ×mol(Zr)$^{-1}$× $[C_nH_{2n}]^{-1}$×h^{-1}; [c] butene content in the copolymer, determined by ^{13}C NMR; [d] average copolymerization degree determined by ^{1}H NMR based on the concentration of chain end groups.

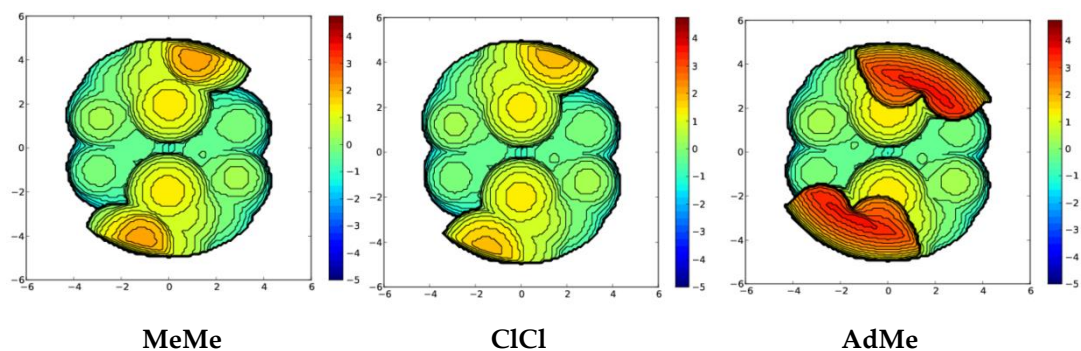- **Buried volume analysis**

| MeMe | ClCl | AdMe |

Figure S1. Steric heat maps from buried volume analysis for catalysts **MeMe** and **ClCl** (see also Table 3). **AdMe** given for comparison

- **Electronic charges**

Table S6. Comparison between DFT estimated Q_{ZrCl2}, experimental r-parameters for ethene/butene copolymerization and corresponding $\Delta\Delta G^{\ddagger}$ (in kcal/mol).

Entry	Catalyst	Q_{ZrCl2}	r_E	r_B	$\Delta\Delta G^{\ddagger}_{(EB-EE)}$	$\Delta\Delta G^{\ddagger}_{(BE-BB)}$
1	**MeMe**	0.874	60	0.012	2.4	-2.6
2	**MeCl**	0.882	38	0.025	2.2	-2.2
3	**ClMe**	0.895	33	0.034	2.1	-2.0
4	**ClCl**	0.904	22	0.06	1.8	-1.7

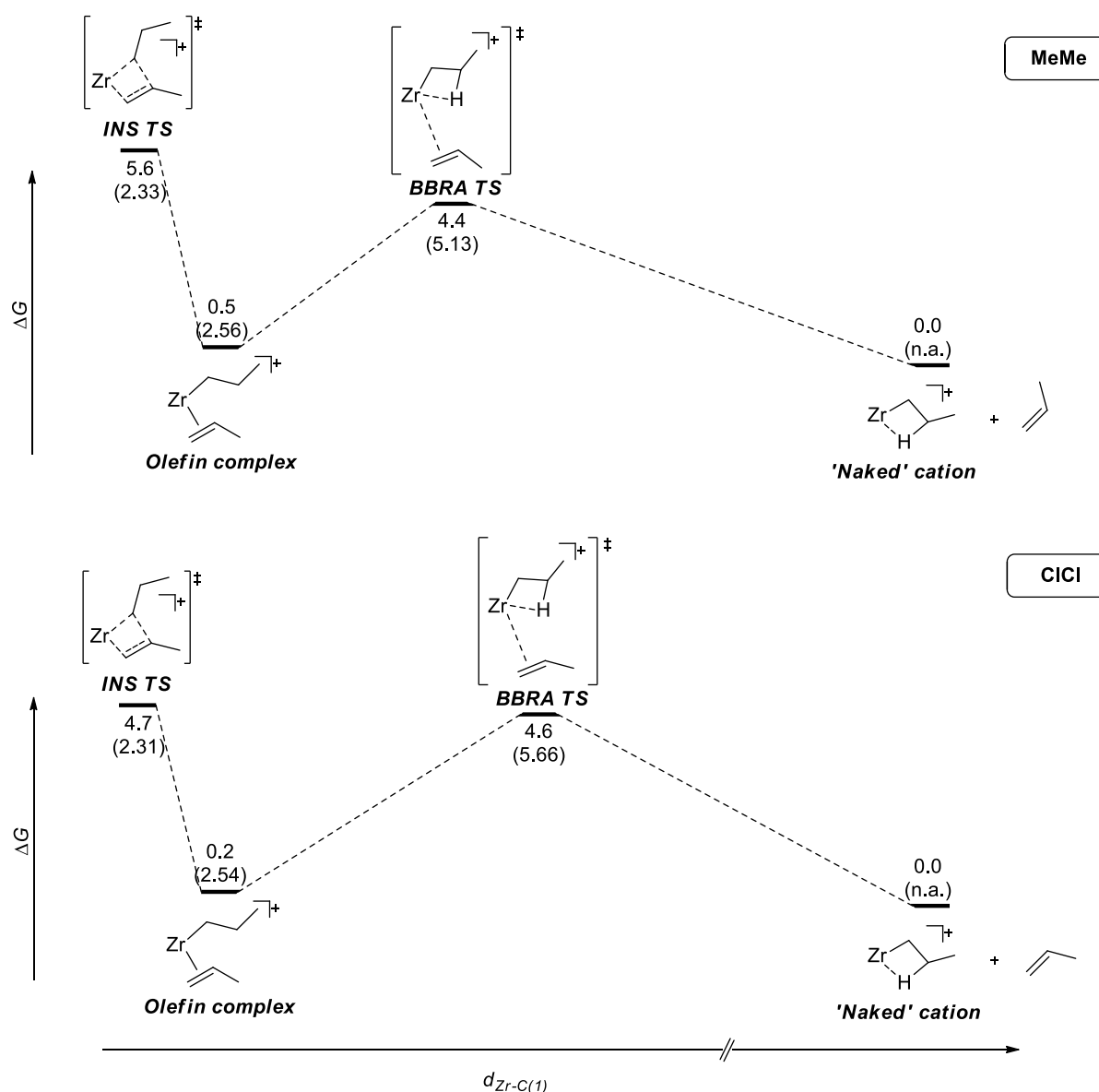- **Calculated reaction profiles for propene enchainment after ethene**

Figure S2. Energies profiles for propene enchainment after ethene predicted by DFT for **MeMe** and **ClCl**. INS = insertion, BBRA = backbone rearrangement. Numbers are relative Gibbs free energy differences in kcal/mol; numbers in brackets are distances between the Zr center and the C(1) carbon of ethene in Å ($d_{Zr-C(1)}$). A Zr-nPr group is used as model for the Zr-polymeryl after ethene insertion (see Materials and Methods).

- **Final energies, entropy and enthalpy corrections in Hartree**

Name	Formula	RI-TPSSTPSS/DZ				M06-2X(PCM)/TZ
		Energy	ZPE	EnthalpyCorr (T=298 K, p=1.0 atm)	EntropyCorr (T=298 K, p=1.0 atm)	Energy
MeMe_ZrCl2	C22H30Cl2N2O2Zr	-2084.361224	0.477314	0.510633	0.097763	-2083.894133
MeCl_ZrCl2	C20H24Cl4N2O2Zr	-2924.962856	0.404720	0.436752	0.093948	-2924.495354
ClMe_ZrCl2	C20H24Cl4N2O2Zr	-2924.956744	0.404516	0.436729	0.095355	-2924.489575
ClCl_ZrCl2	C18H18Cl6N2O2Zr	-3765.554608	0.331533	0.362585	0.092789	-3765.086479
ethene	C2H4	-78.605619	0.050223	0.054225	0.024892	-78.571775
propene	C3H6	-117.933593	0.078307	0.083377	0.030094	-117.883416
MeMe_nPr	C25H37N2O2Zr	-1282.106400	0.566008	0.600650	0.099172	-1281.645679
MeMe_ethene_nPr	C27H41N2O2Zr	-1360.723808	0.618557	0.657048	0.107795	-1360.226474
MeMe_propene_nPr	C28H43N2O2Zr	-1400.052269	0.645664	0.685861	0.111962	-1399.541741
MeMe_ethene_nPr_BBRA_TS	C27H41N2O2Zr	-1360.714884	0.616755	0.655883	0.113782	-1360.219590
MeMe_ethene_nPr_INS_TS	C27H41N2O2Zr	-1360.723311	0.619147	0.656602	0.105638	-1360.225028
MeMe_propene_nPr_BBRA_TS	C28H43N2O2Zr	-1400.043321	0.644616	0.684973	0.117252	-1399.531010
MeMe_propene_nPr_INS_TS	C28H43N2O2Zr	-1400.047796	0.647068	0.685808	0.108139	-1399.536178
MeMe_ethene_iBu_BBRA_TS	C28H43N2O2Zr	-1400.038550	0.644204	0.684735	0.116505	-1399.530246
MeMe_ethene_iBu_INS_TS_A	C28H43N2O2Zr	-1400.045024	0.646559	0.685332	0.107834	-1399.534608
MeMe_ethene_iBu_INS_TS_B	C28H43N2O2Zr	-1400.043060	0.646499	0.685301	0.108207	-1399.531223
MeMe_propene_iBu_BBRA_TS	C29H45N2O2Zr	-1439.366693	0.672107	0.713804	0.118956	-1438.841650
MeMe_propene_iBu_INS_TS_A	C29H45N2O2Zr	-1439.369398	0.674395	0.714475	0.110302	-1438.845527
MeMe_propene_iBu_INS_TS_B	C29H45N2O2Zr	-1439.366465	0.674487	0.714550	0.110697	-1438.842006
ClCl_nPr	C21H25Cl4N2O2Zr	-2963.289346	0.420107	0.452528	0.095541	-2962.832557
ClCl_ethene_nPr	C23H29Cl4N2O2Zr	-3041.909112	0.472799	0.509033	0.103821	-3041.414210
ClCl_propene_nPr	C24H31Cl4N2O2Zr	-3081.238086	0.499872	0.537787	0.107650	-3080.729588
ClCl_ethene_nPr_BBRA_TS	C23H29Cl4N2O2Zr	-3041.897581	0.470831	0.507723	0.109791	-3041.405952
ClCl_ethene_nPr_INS_TS	C23H29Cl4N2O2Zr	-3041.908850	0.473239	0.508483	0.101481	-3041.413409
ClCl_propene_nPr_BBRA_TS	C24H31Cl4N2O2Zr	-3081.226092	0.498684	0.536829	0.113516	-3080.717690
ClCl_propene_nPr_INS_TS	C24H31Cl4N2O2Zr	-3081.233760	0.501232	0.537736	0.104123	-3080.724799
ClCl_ethene_iBu_BBRA_TS	C24H31Cl4N2O2Zr	-3081.221779	0.498307	0.536565	0.112165	-3080.717024
ClCl_ethene_iBu_INS_TS_A	C24H31Cl4N2O2Zr	-3081.230867	0.500619	0.537195	0.103939	-3080.722936
ClCl_ethene_iBu_INS_TS_B	C24H31Cl4N2O2Zr	-3081.228788	0.500535	0.537182	0.104653	-3080.719601

- **Full Gaussian citation**

Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.