Cation-Anion Interactions in the Post-Metallocene Olefin Polymerization Catalysts

Zygmunt Flisak* and Akinobu Shiga**

*Uniwersytet Opolski, Wydział Chemii, Oleska 48, 45-052 Opole
**LUMMOX Research Lab, Takezono 2-18-4-302, Tsukuba 305-0032, Japan
zgf@uni.opole.pl

01.03.2013

Contents

Is it worth working on?

"The awarding of the Nobel Prize for Chemistry for the year 1963 is related to the precipitous expansion of macromolecular chemistry and its industrial applications, which began precisely ten years ago [...]"

Ziegler, K., Nobel Lecture, 12.12.1963

Is it worth working on?

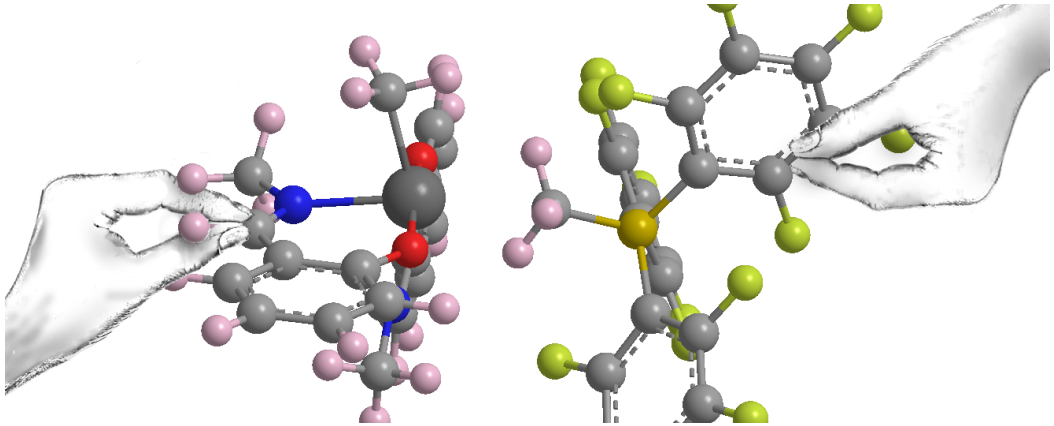
"The awarding of the Nobel Prize for Chemistry for the year 1963 is related to the precipitous expansion of macromolecular chemistry and its industrial applications, which began precisely ten years ago [...]"

Ziegler, K., Nobel Lecture, 12.12.1963

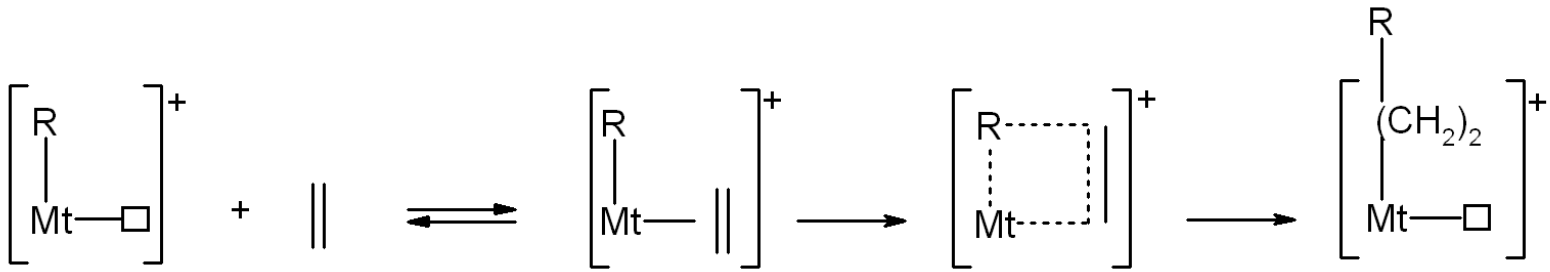
"I have little doubts that an unbiased reader [...] cannot but conclude that catalytic olefin polymerization is by far the most advanced area of non-natural selective chemical synthesis, uniquely combining a thorough molecular control and a gigantic application scale, and at the same time that it continues to produce breakthroughs."

Busico, V., *Macromol. Chem. Phys.* 2007, 208, 26

Catalytic ion pair

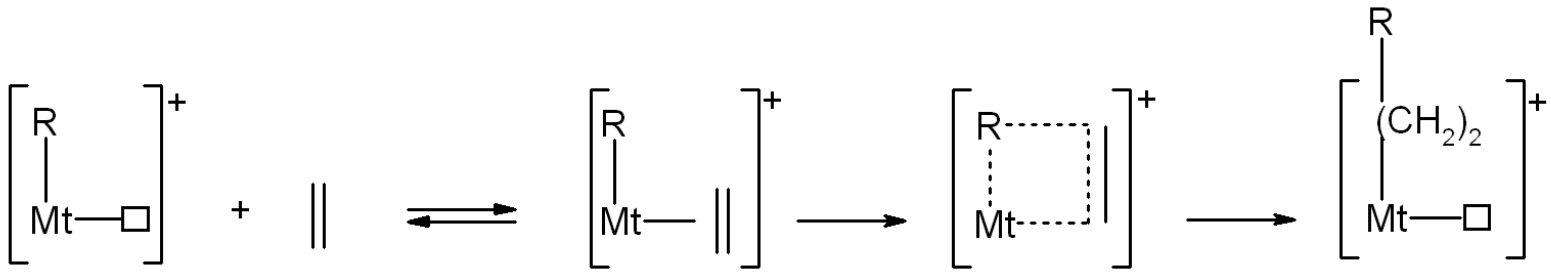


Polymerization Mechanism: two barriers

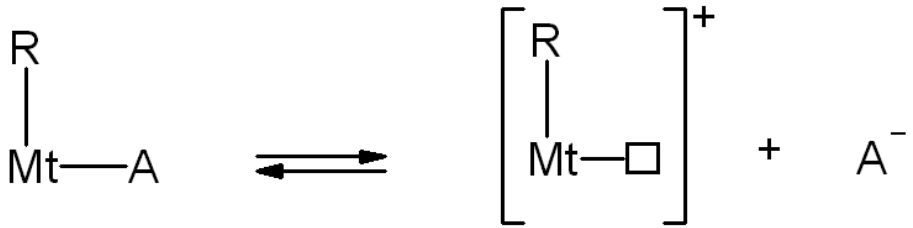


Olefin insertion

Polymerization Mechanism: two barriers



Olefin insertion



Counter ion separation

The two barriers compared

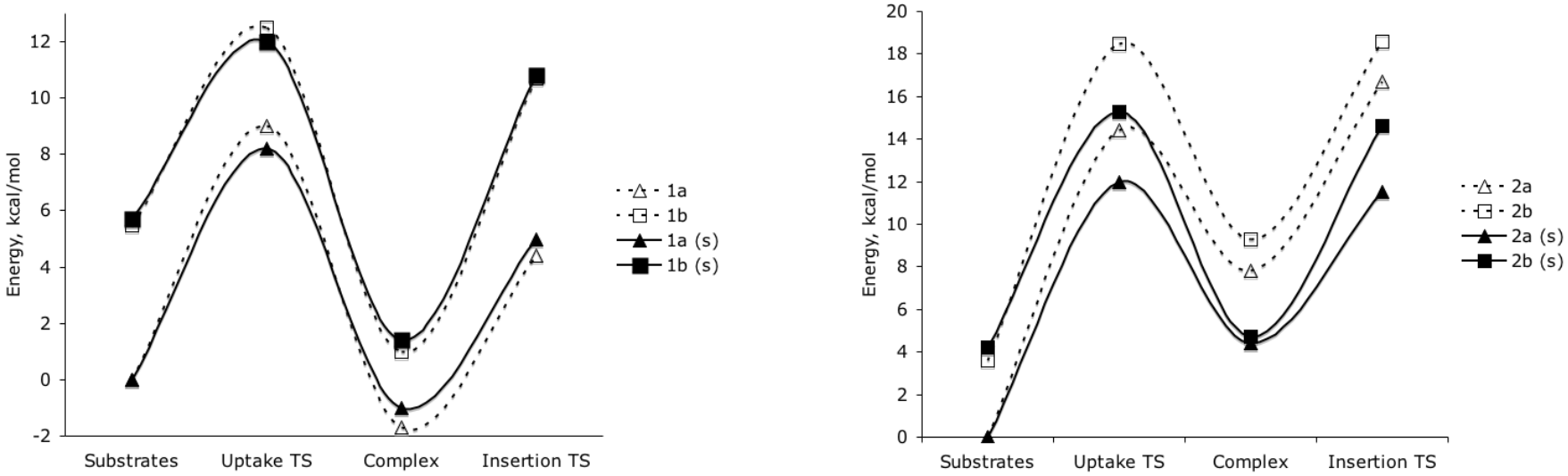
Catalyst	Separation barrier	Insertion barrier	Ref.
Phosphonimide	41.6	—	1
Pyrrolide-imine	12.9*	3.8	2
Metallocene	12.0*	7.0	3
Salan	8.0*	6.0	3

* including olefin uptake

1. Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* 2002, 21, 2444.
2. Vanka, K.; Xu, Z.; Ziegler, T. *Organometallics* 2004, 21, 2900.
3. Flisak, Z.; Ziegler, T. *Proc. Natl. Acad. Sci. U.S.A.* 2006, 103, 15338.

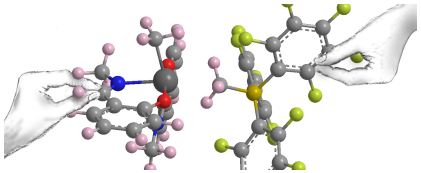
Counteranion Separation vs. Catalytic Activity

Postmetallocene (1) and metallocene (2)



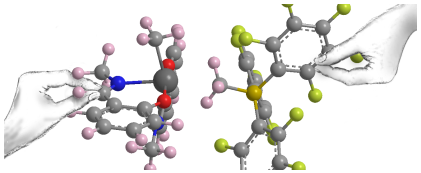
Flisak Z.; Ziegler T., *Proc. Natl. Acad. Sci. USA* 2006, 103, 15338.

Ion pair separation

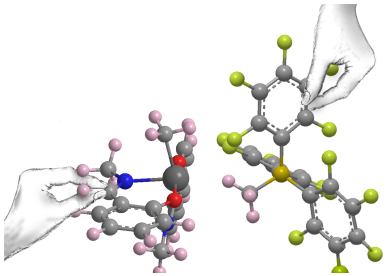


Starting point

Ion pair separation

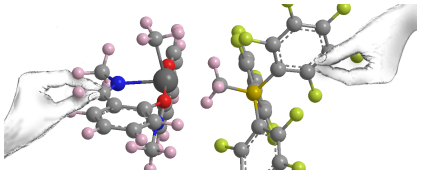


Starting point

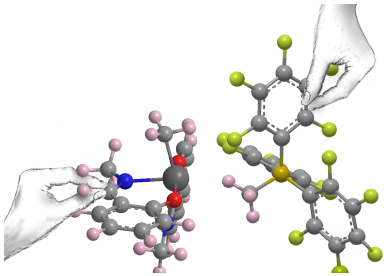


Separation to the second coordination sphere

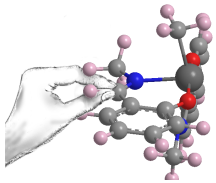
Ion pair separation

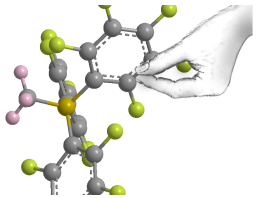


Starting point



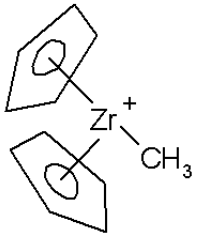
Separation to the second coordination sphere

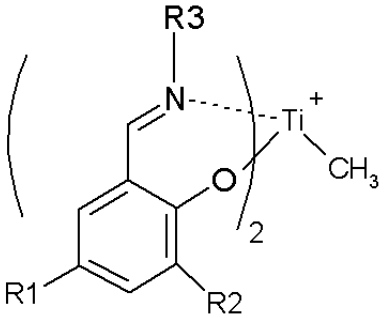


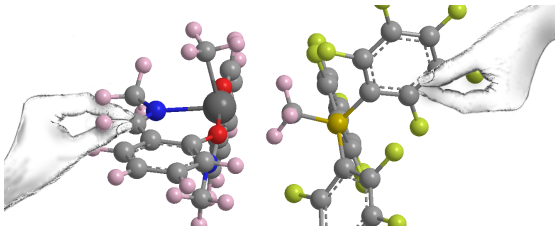


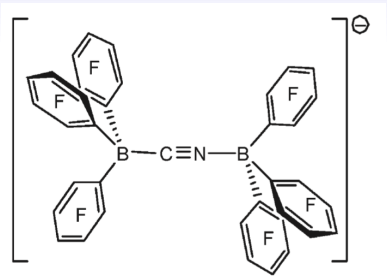
Separation to infinity

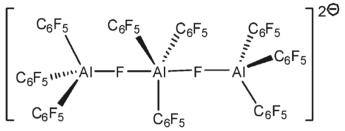
Counteranion tuning

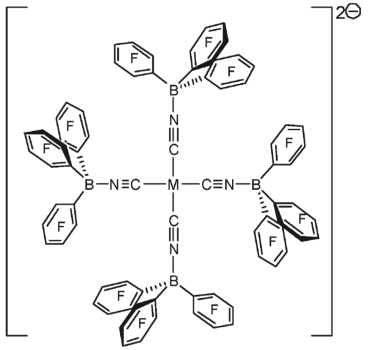








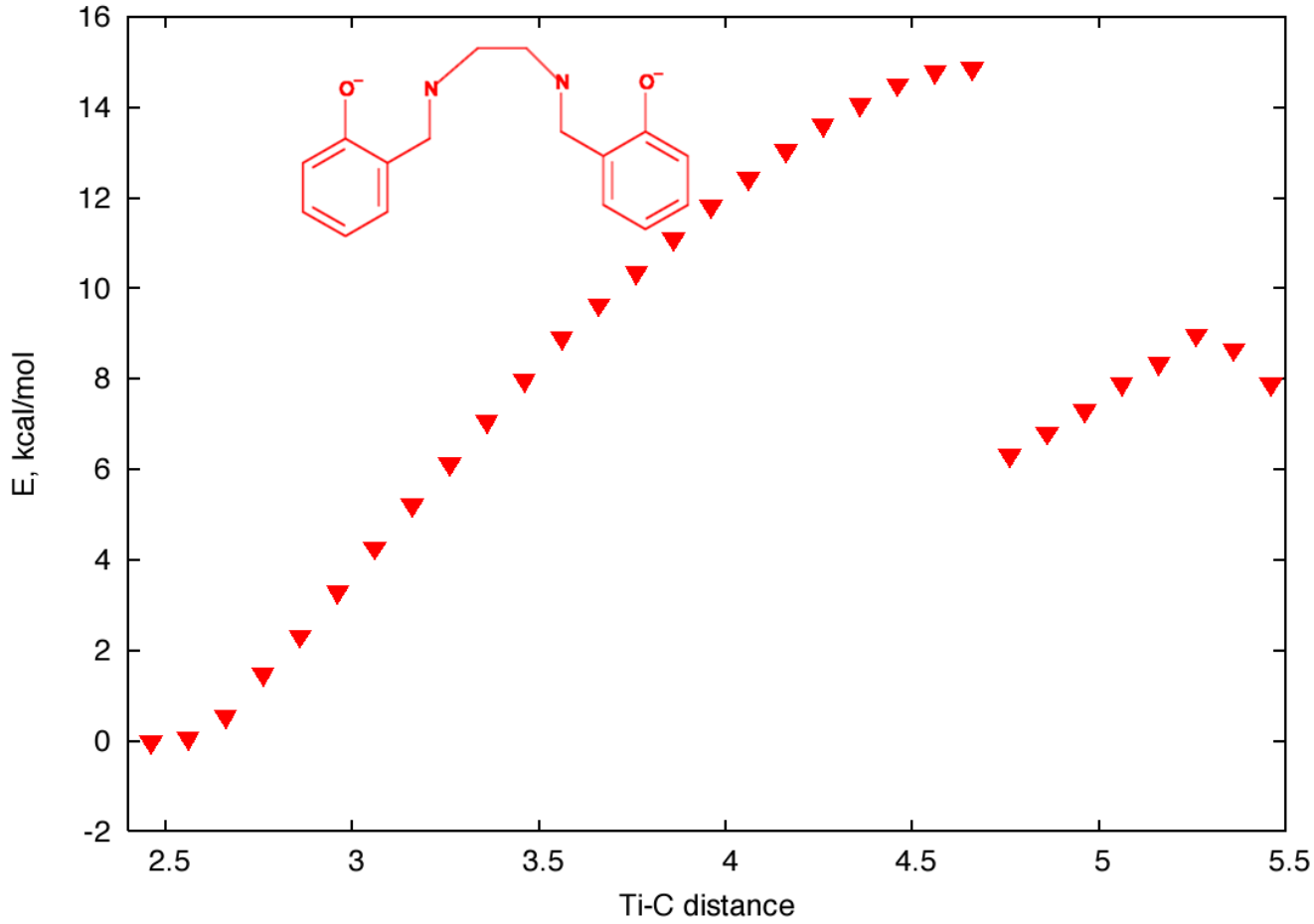




M = Ni, Pd

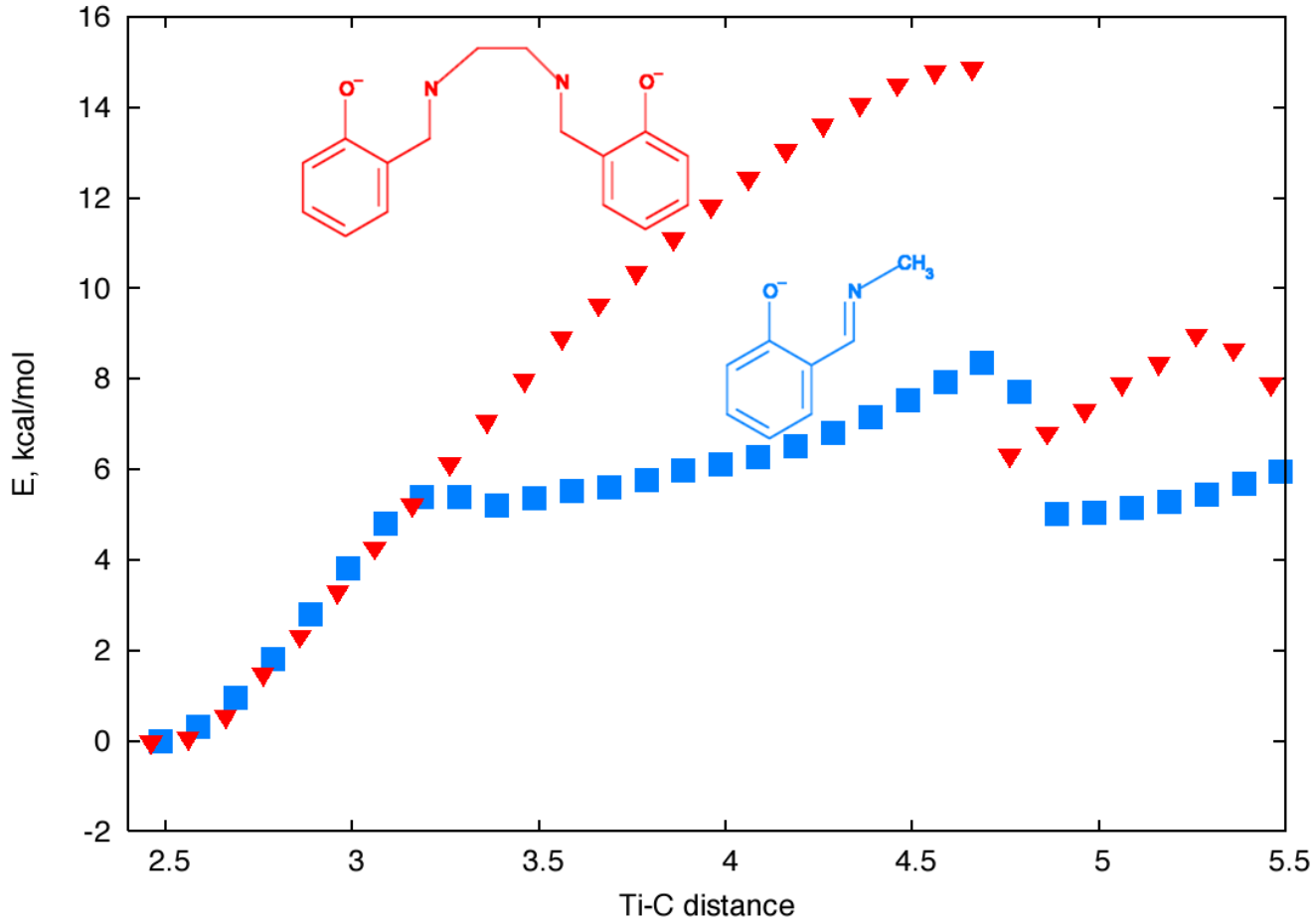
Bochmann, M, *Organometallics* 2010, 29, 4711

Separation to the 2nd Coordination Sphere



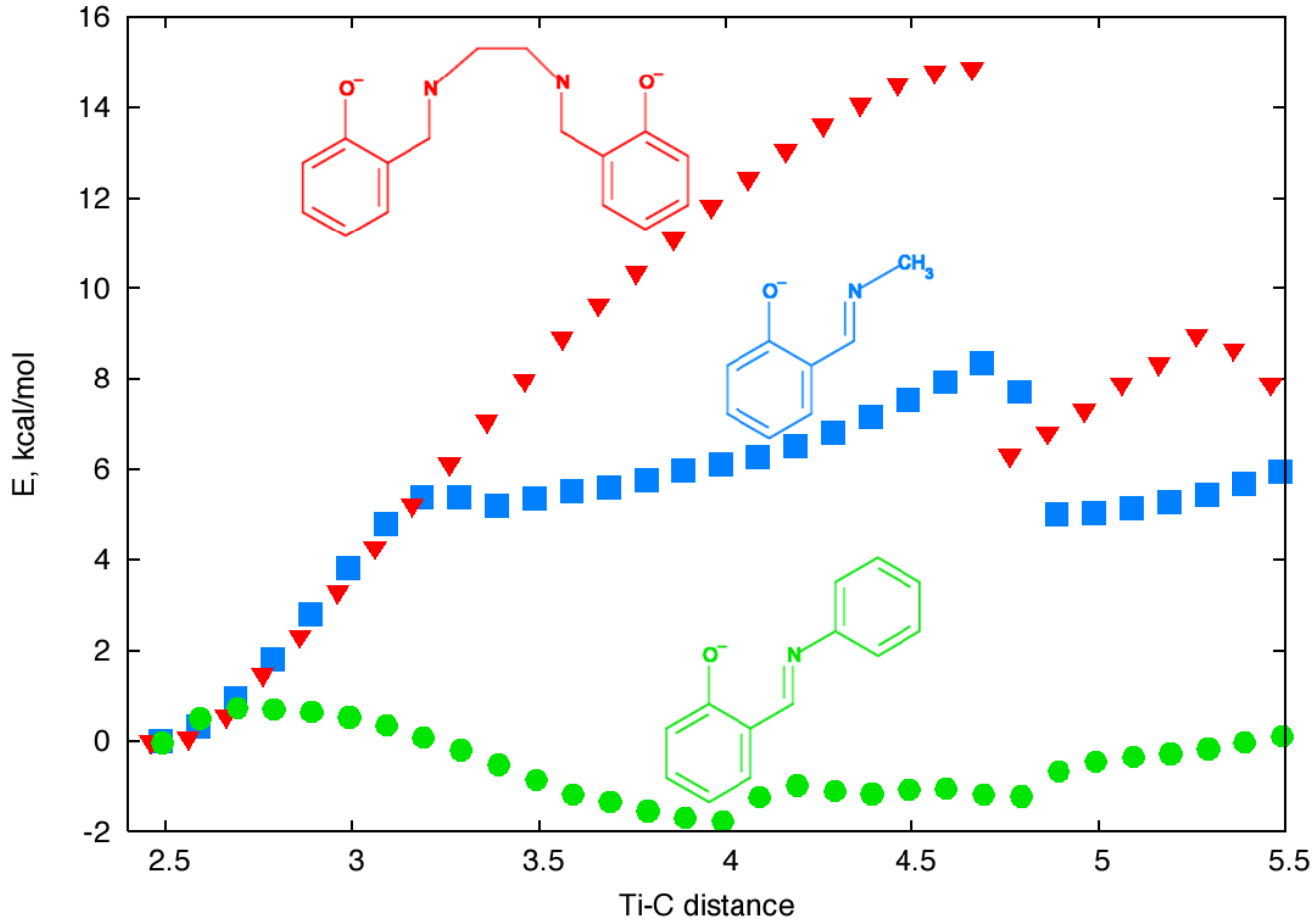
Flisak, Z.; Suchorska, P., *Organometallics* 2010, 29, 6196.

Separation to the 2nd Coordination Sphere



Flisak, Z.; Suchorska, P., *Organometallics* 2010, 29, 6196.

Separation to the 2nd Coordination Sphere



Flisak, Z.; Suchorska, P., *Organometallics* 2010, 29, 6196.

Separation to infinity

Cation-anion (M-C) distance and separation energies (E_{sep}) for the selected Ti ion pairs

Ligand	M-C distance,		E_{sep}, kcal/mol	
	DFT	DFT-D3	DFT	DFT-D3
indenyl	2.438	2.368	70.98	97.74
salan	2.455	2.414	65.01	90.40
FI-Ph	2.464	2.417	45.43	80.38
FI-Me	2.485	2.451	50.36	76.37

Flisak, Z.; Shiga, A, *J. Organomet. Chem.* 2012, 718, 124

Can phenoxyimine ligands donate charge?

Charge analysis in the titanium catalysts

Ligand	Ti^{4+}	$L_1^- + L_2^-$
	precursor	
indenyl	2.7481	-1.2419
salan	2.9017	-1.2928
FI-Ph	2.9248	-1.3717
FI-Me	2.9365	-1.3854
	ion pair	
indenyl	2.6361	-1.0576
salan	2.8052	-1.1391
FI-Ph	2.8520	-1.1964
FI-Me	2.8491	-1.2415

Flisak, Z.; Shiga, A, *J. Organomet. Chem.* 2012, 718, 124 Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T., *Organometallics* 2002, 21, 2444

What is the dominant type of interactions?

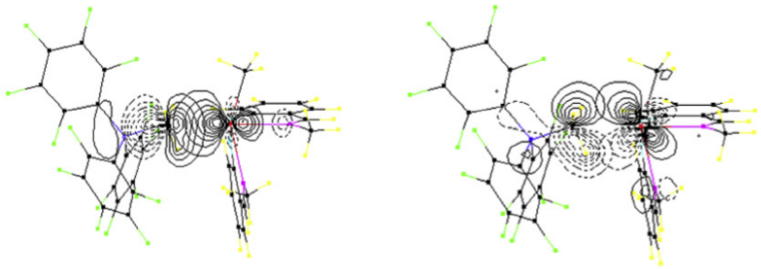
Energy decomposition into repulsive (Pauli) and attractive (electrostatic as well as orbital) interactions, kcal/mol

Morokuma, K, *J. Chem. Phys.* 1971, 55, 1236
Ziegler, T.; Rauk, A, *Theor. Chim. Acta* 1977, 46, 1

Ligand	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}
indenyl	57.53	-93.32	-44.61
salan	51.75	-85.03	-40.14
FI-Ph	55.65	-83.79	-42.53
FI-Me	50.09	-84.17	-38.01

Flisak, Z.; Shiga, A, *J. Organomet. Chem.* 2012, 718, 124

Paired Interacting Orbitals



Fujimoto, H., *Acc. Chem. Res.* 1987, 20, 448

Overlap population of PIO-1 and PIO-2 for each model

Ligand	PIO-1	PIO-2	Σ OP
indenyl	0.1482	0.0628	0.2110
salan	0.1068	0.0850	0.1918
FI-Ph	0.0798	0.1179	0.1977
FI-Me	0.1016	0.0695	0.1711

Flisak, Z.; Shiga, A, *J. Organomet. Chem.* 2012, 718, 124

Conclusions

- Phenoxyimine-based catalysts activated with perfluorophenylborate exhibit very low ion separation barrier, which may contribute to their unprecedented activity;
- Electrostatic interactions constitute 70% of the energy of all attractive interactions;
- Ligands donate negative charge to weaken cation-anion interactions;
- PIO analysis is in good agreement with DFT results.

Acknowledgment

CYFRONET 

WCSS 

Thank you for your kind attention