DPI Golden Thesis Award

NMR Studies on Metallocene Ion Pairs Relevant to Catalytic Olefin Polymerization

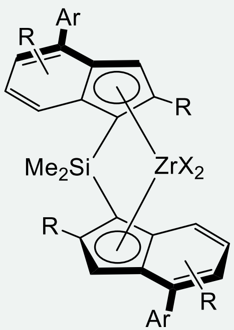
Annual DPI Meeting
Eindhoven, 27 October 2020

PhD
Leonardo Sian

Supervisors
Prof. Alceo Macchioni
Prof. Cristiano Zuccaccia

DPI Project #800

Quantitative Structure – Activity Relationships (QSAR) in Metallocene-Based Olefin Polymerization Catalysis

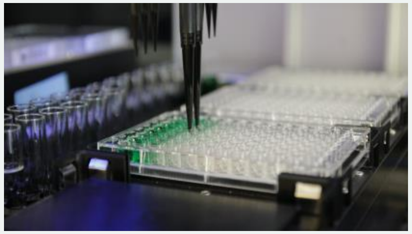


Moscow State University

University of Perugia

DPI Project #800b

University of Naples



Summary of the Talk

1) Introduction: Ion pairing in olefin polymerization

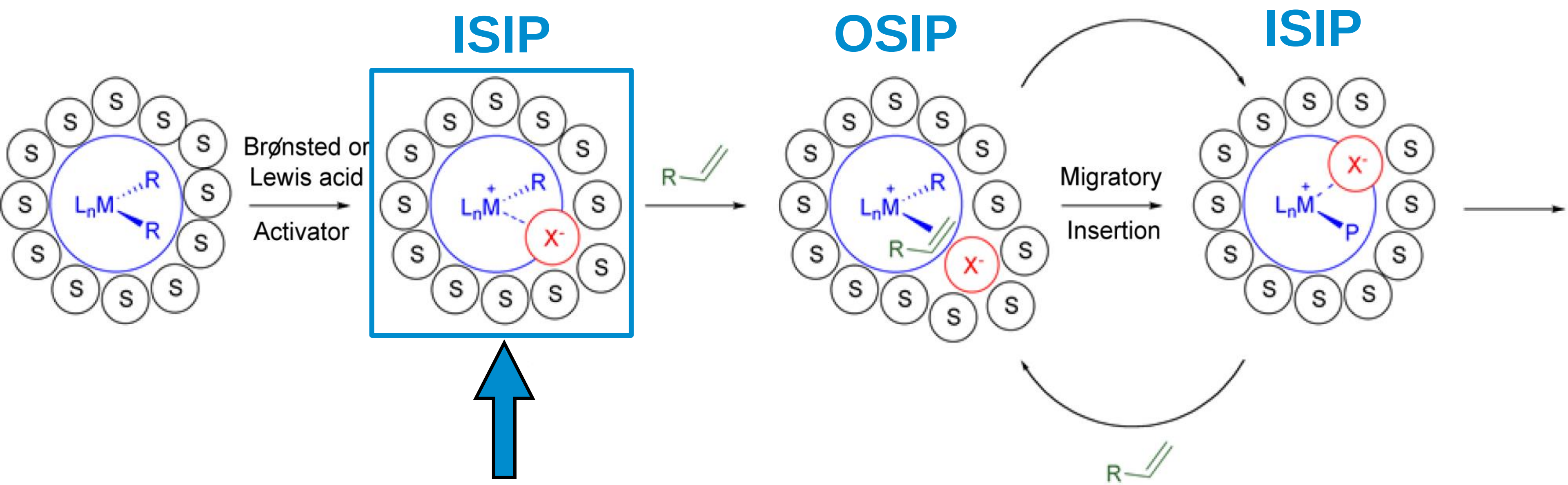
2) Kinetic effect of ion aggregates on the rate of olefin insertion

3) Solvent coordination on *ansa*-metallocene catalysts

4) Application of complementary techniques to industrially relevant catalytic systems activated with Methylaluminoxane (SABIC)

Ion Pairs in Homogenous Olefin Polymerization

Cossee-Arlman mechanism



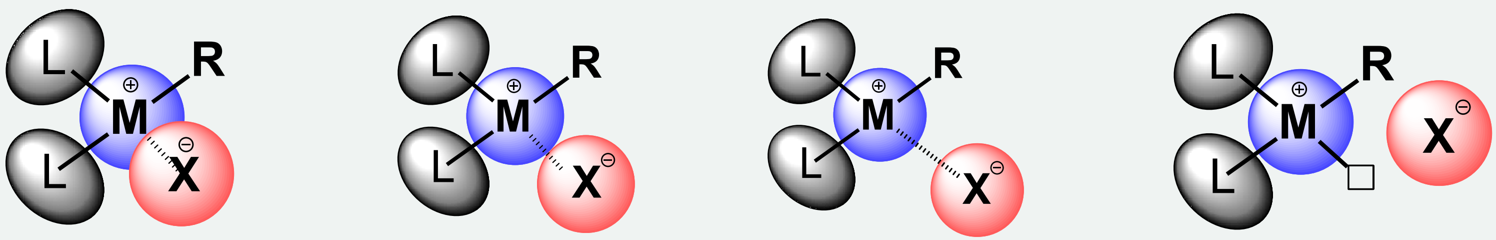
Electrostatic cation-anion interactions play a crucial role

Inner Sphere Ion Pair (ISIP) *vs* Outer Sphere Ion Pair (OSIP)

Brintzinger, *Organometallics* **2002**, *21*, 473; Bochmann, *J. Organomet. Chem.* **2004**, *689*, 3982; Macchioni, *Chem. Rev.* **2005**, *105*, 2039.

Modulation of Cation – Anion Interaction

Cation engineering | **Anion engineering** | **Solvent or temperature**



Tight - ISIP | **Loose - ISIP** | **OSIP**

→ **Cation-anion interaction strength in ion pairs**

← **Ion pair stability**

→ **Catalytic activity**

→ **Self-aggregation tendency of ion pairs** … **Solvent coordination**

Chen and Marks, *Chem. Rev.* **2000**, *100*, 131; Macchioni, *Chem. Rev.* **2005**, *105*, 2039; Bochmann, *Organometallics* **2010**, *29*, 4711.

Summary of the Talk

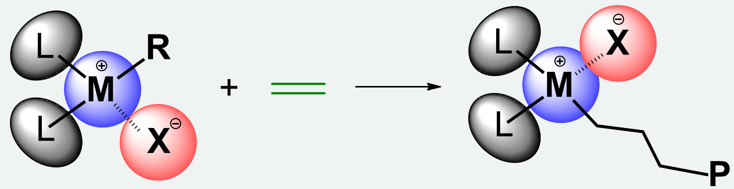
1) Introduction: Ion pairing in olefin polymerization

2) Kinetic effect of ion aggregates on the rate of olefin insertion

3) Solvent coordination on *ansa*-metallocene catalysts

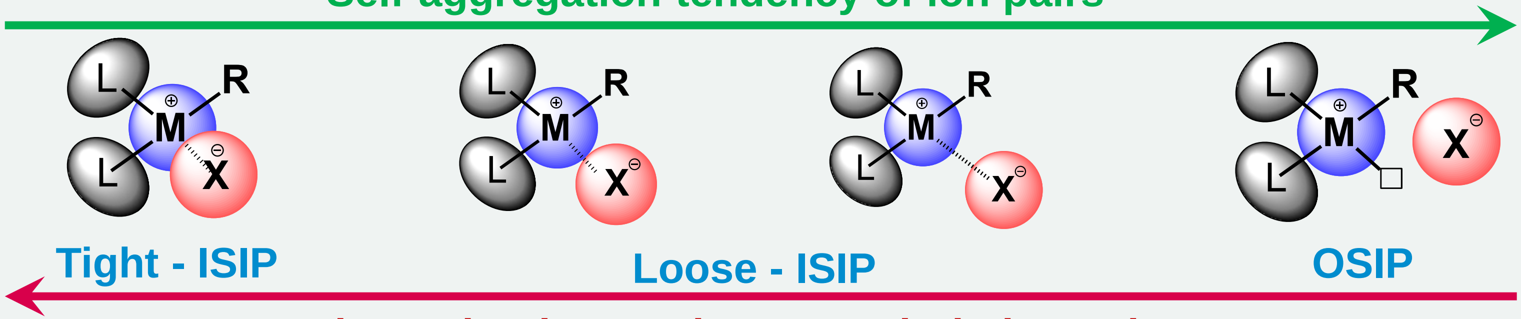
4) Application of complementary techniques to industrially relevant catalytic systems activated with Methylaluminoxane (SABIC)

Linking Thermodynamics of Ion Aggregation with Kinetics of Olefin Insertion



Kinetic Effect?

Self-aggregation tendency of ion pairs



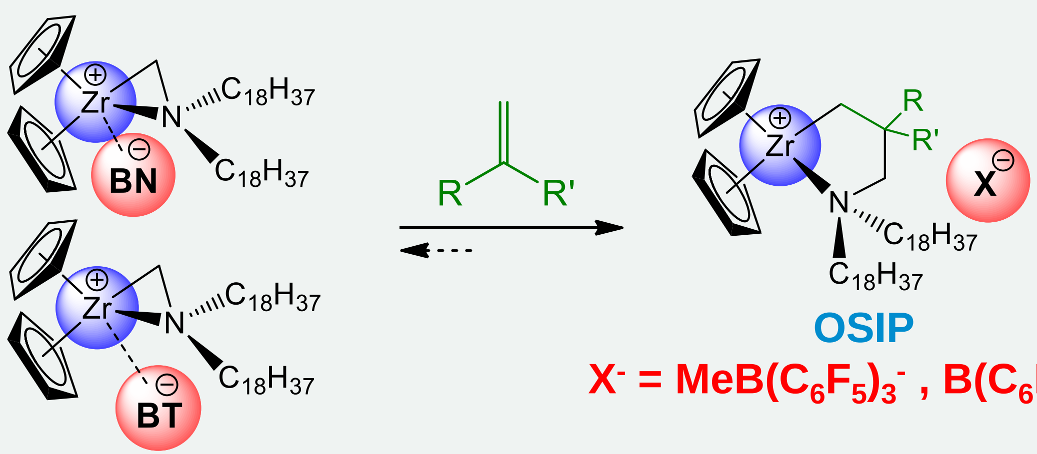
Cation-anion interaction strenght in ion pairs

Tight - ISIP

$BN^- = MeB(C_6F_5)_3^-$

Loose - ISIP

$BT^- = B(C_6F_5)_4^-$

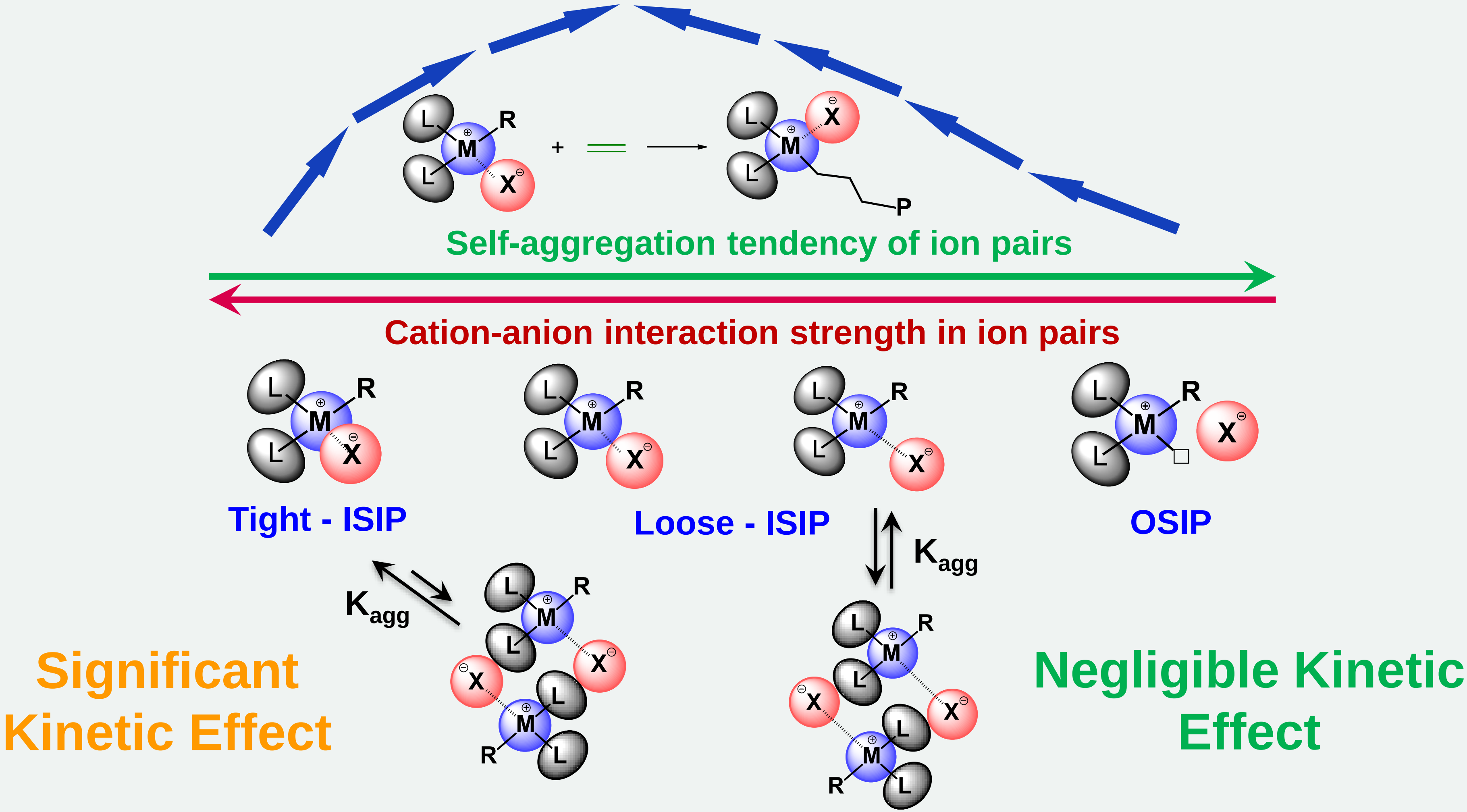


OSIP

$X^- = MeB(C_6F_5)_3^-$, $B(C_6F_5)_4^-$

Chem. Eur. J. ***2008***; *Organometallics* **2011**, 100; *Angew. Chem. Int. Ed.* **2011**, 50; *J. Organomet. Chem.* **2012**.

Kinetic Relevance of Ion Aggregates on Olefin Insertion Process



Quantitative structure – activity relationship, linking for the first time the self-aggregation tendency of ion pairs with the kinetic of olefin insertion into metal-carbon bond.

ACS Catalysis **2020**, *10*, 1591 .

Summary of the Talk

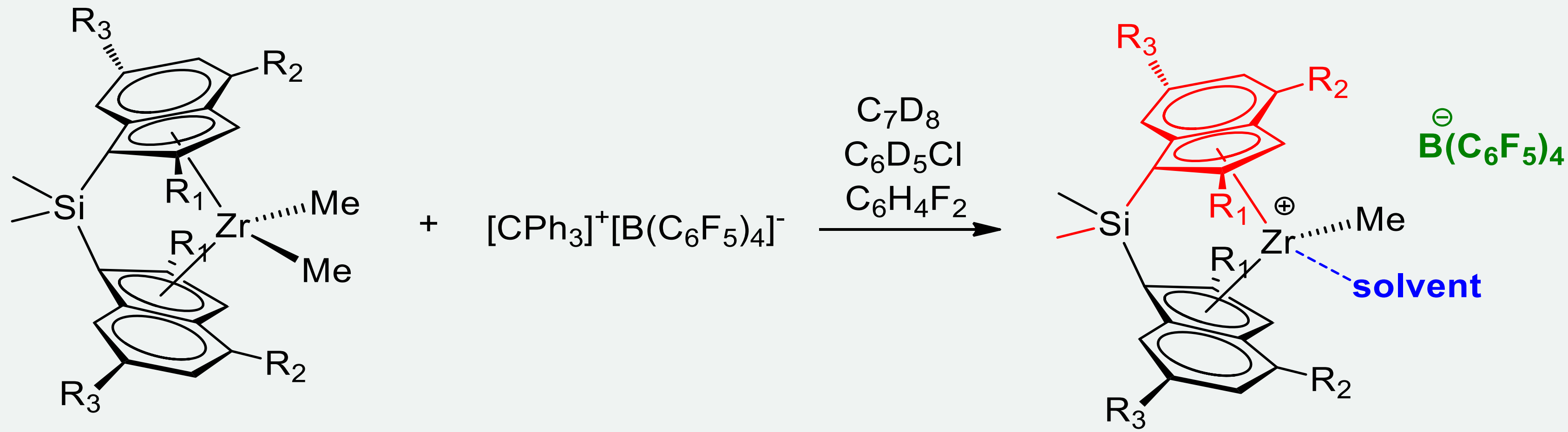
1) Introduction: Ion pairing in olefin polymerization

2) Kinetic effect of ion aggregates on the rate of olefin insertion

3) Solvent coordination on *ansa*-metallocene catalysts

4) Application of complementary techniques to industrially relevant catalytic systems activated with Methylaluminoxane (SABIC)

Activation of Catalytically Relevant Ansa-Metallocenes

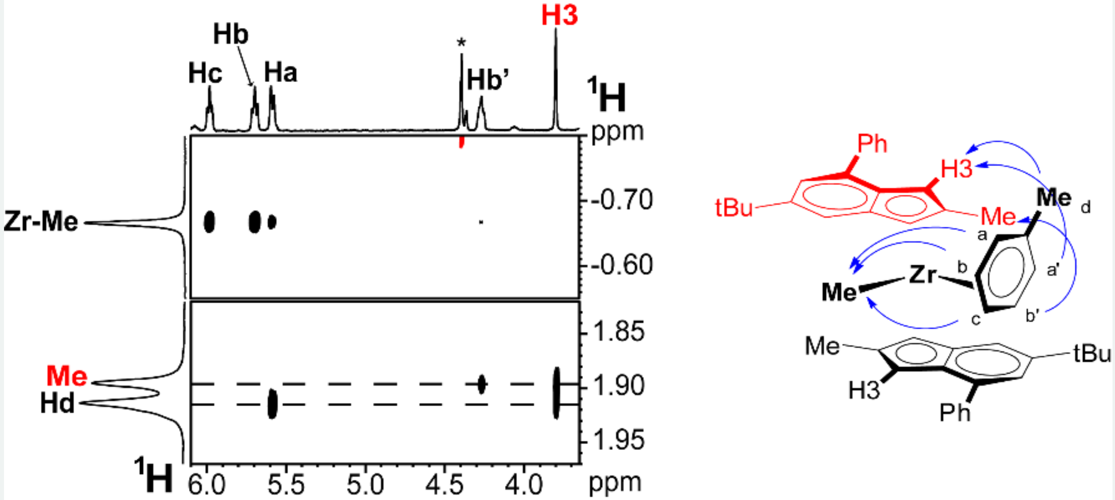


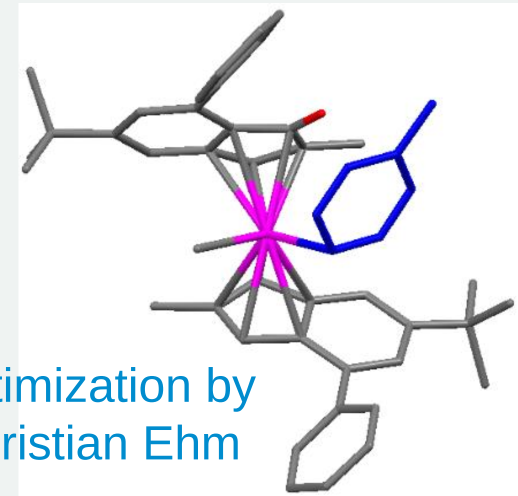
1: R_1=Me, R_2=Ph, R_3=t-bu
2: R_1=Me, R_2=Me, R_3=H
3: R_1=H, R_2=H, R_3=H

1BT: R_1=Me, R_2=Ph, R_3=t-bu
2BT: R_1=Me, R_2=Me, R_3=H
3BT: R_1=H, R_2=H, R_3=H

- *Different cations but same counterion (**BT**)*
- *Activator: Trityl-borate*
- *Different solvents (C_7D_8, C_6D_5Cl, $C_6H_4F_2$)*

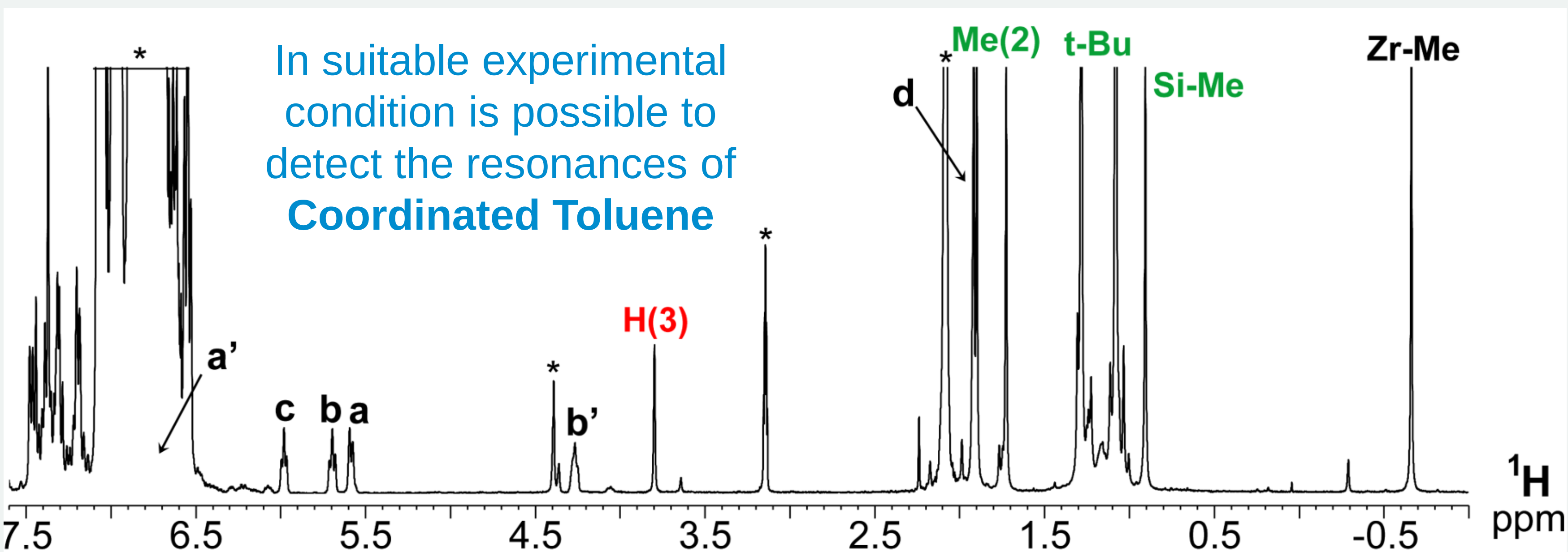
Direct evidence for solvent coordination





Optimization by Christian Ehm

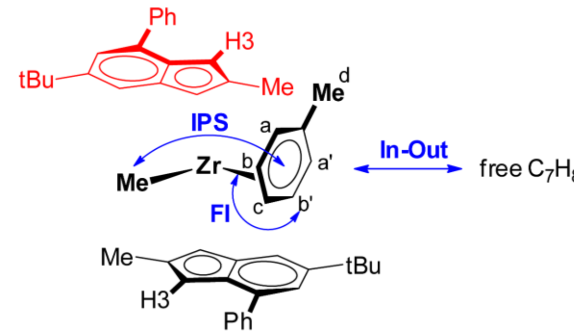
In suitable experimental condition is possible to detect the resonances of **Coordinated Toluene**



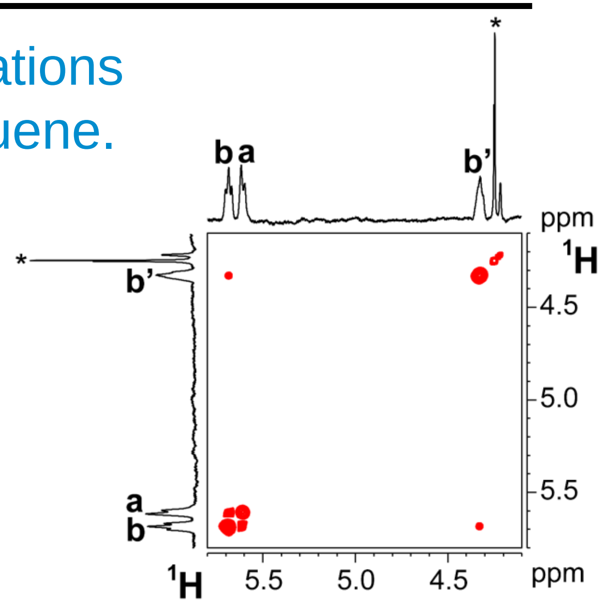
Dynamics of Coordinated Toluene

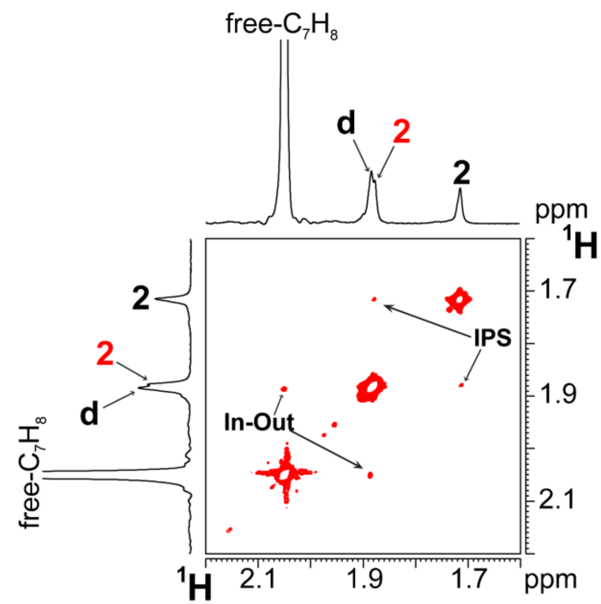
3 different motions

Motion	k (253K) (s^{-1})	$\Delta H^{\neq}$ (Kcal/mol)	$\Delta S^{\neq}$ (cal/mol)	$\Delta G^{\neq}$ (298K) (Kcal/mol)
In - Out	0.71	15.9	3.8	14.8
Face Inv	14.2	14.6	4.6	13.2
IPS	0.14	18.5	11.3	15.1



Homogenous polymerizations are often carried out in toluene.





The aspect of solvent coordination at metal centre may help to rationalize the catalytic behaviour of this class of catalysts.

Summary of the Talk

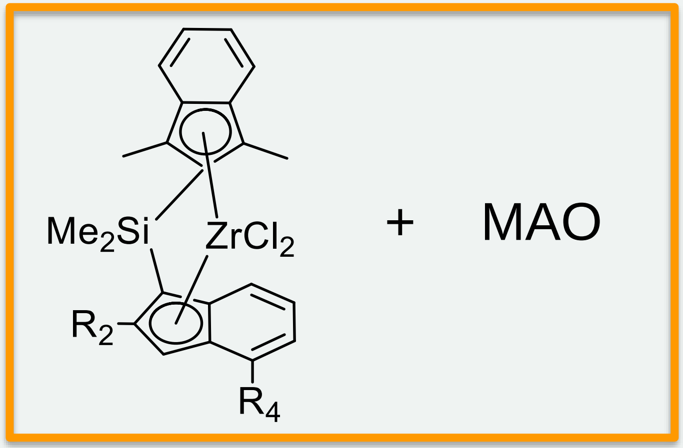
1) Introduction: Ion pairing in olefin polymerization

2) Kinetic effect of ion aggregates on the rate of olefin insertion

3) Solvent coordination on *ansa*-metallocene catalysts

4) Application of complementary techniques to industrially relevant catalytic systems activated with Methylaluminoxane (SABIC)

Advantages of UV-Vis Spectroscopy

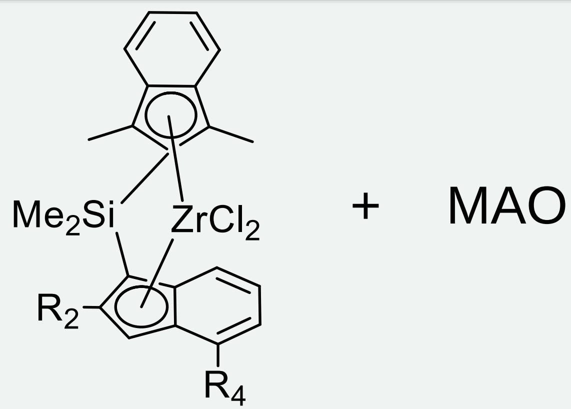


- LMCT bands
- MAO is transparent
- Fast analysis
- High sensitivity
- Industrial condition
- Less Informative

Combined Approach to study the Activation with MAO

UV-vis spectroscopy

- LMCT bands
- MAO is transparent
- Fast analysis
- High sensitivity
- Industrial condition



NMR spectroscopy

- Synthesis and characterization of well defined species
- Comparison of UV-vis spectra

DFT

- Well defined species
- Predictive UV-vis spectra

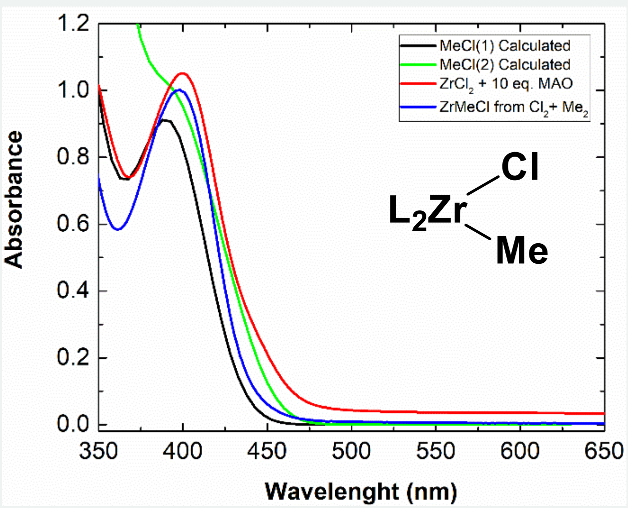
Combined Approach to study the Activation with MAO

DPI
The Polymer Research Platform

Experiments (NMR and UV-vis)

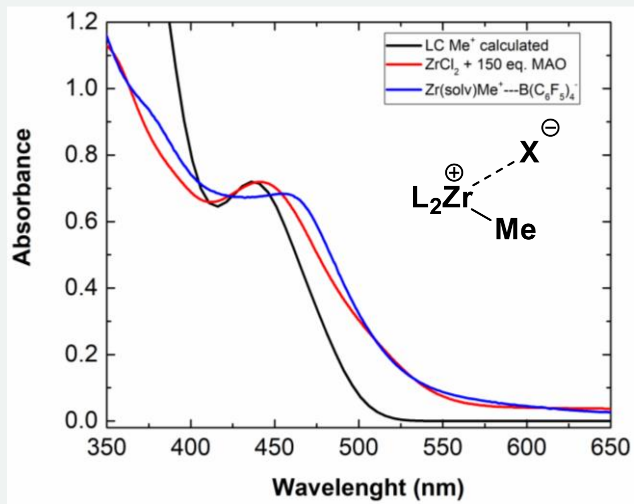
DFT Calculation (Prediction of UV-vis spectra)

Cl_2 + MAO (10 eq.)



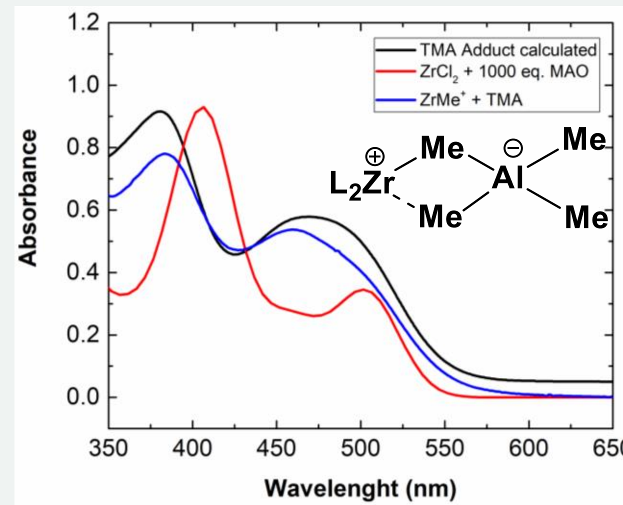
Cl_2 + Me_2

Cl_2 + MAO (150 eq.)



Me_2 + trityl-borate

Cl_2 + MAO (1000 eq.)



Me_2 + trityl-borate + TMA

The experimental trends of dichlorides activated with different equivalents of MAO are well reproduced by DFT calculations and experiments carried out on well-defined species.

سابك
sabic

Activation in homogenous phase

(92)$ZrCl_2$: R_2= H, R_4= H

(95)$ZrCl_2$: R_2= Me, R_4= H

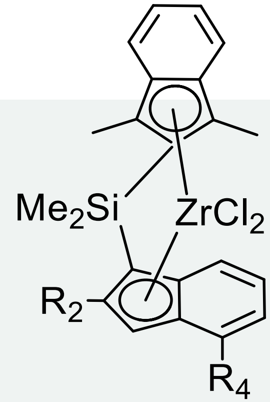
(121)$ZrCl_2$: R_2= *i*-Pr, R_4= H

(150)$ZrCl_2$: R_2= *t*-Bu, R_4= H

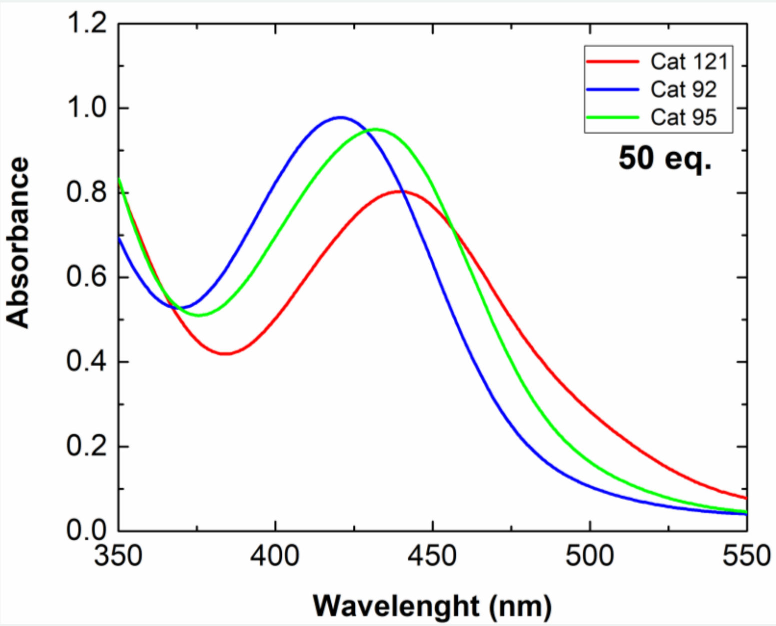
(93)$ZrCl_2$: R_2= Ph, R_4= H

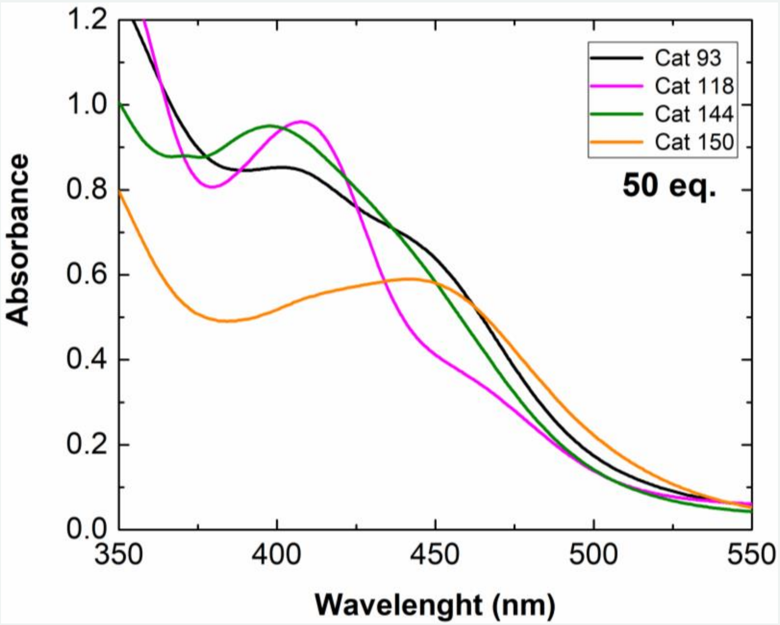
(118)$ZrCl_2$: R_2= Ph, R_4= Ph

(144)$ZrCl_2$: R_2= Ph, R_4= Benz[e]Ind



+ MAO

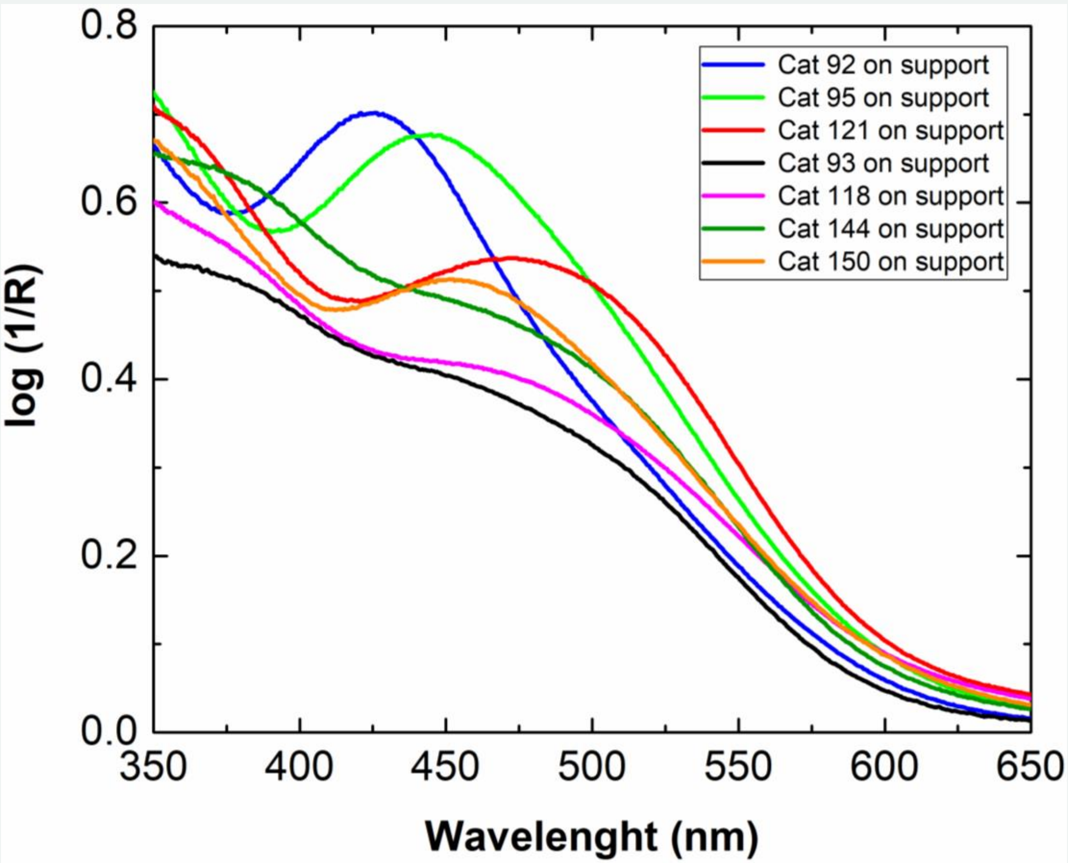


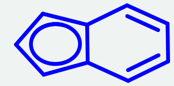


- *UV-vis spectra in **homogenous phase** revealed a catalysts early activation (ca. 50 eq. MAO) with small alkyl substituents in position 2 (high activity).*
  Late activation (ca. 150 eq. MAO) was observed for sterically demanding substituents (low activity).

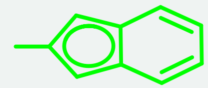
Ansa-Metallocenes + MAO on support

The Polymer Research Platform

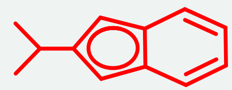




(92)$ZrCl_2$

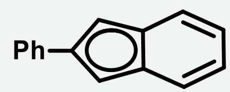


(95)$ZrCl_2$

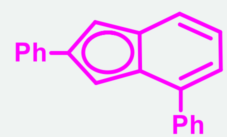


(121)$ZrCl_2$

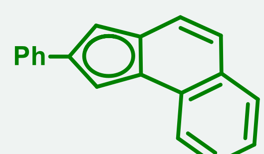
(150)$ZrCl_2$



(93)$ZrCl_2$



(118)$ZrCl_2$



(144)$ZrCl_2$

Increase of substitution hindrance

Broadening increase in transformed reflective spectra

Decrease of catalysts activity

Conclusions

1) Demonstration of the kinetic relevance of ion aggregates on the olefin insertion process.

2) *Ansa*-Metallocenes in combination with molecular activator revealed an unprecedent solvent coordination at metal center.

3) UV-vis spectroscopy can be used as a predictive tool to study the activation of *ansa*-metallocenes with MAO and the use of different complementary techniques allows to determine catalysts speciation and correlate *catalytic performances* - *activation process* - *ligand functionalization*.

Acknowledgements

DPI
The Polymer Research Platform

سابك
sabic

STUDIUM GENERALE CIVITATIS PERUSII
A.D. MCCCVIII

Dipartimento di Chimica, Biologia e Biotecnologie
Università degli Studi di Perugia
DIPARTIMENTO di ECCELLENZA 2018 2022

1755

FRIDERICUS II IMPERATOR ROMANORUM SEMPER AUGUSTUS

Thank for your kind attention!