



HAL
open science

Investigation of Catalytic Dehydrocoupling of Dimethylamine-borane by Titanocene: A DFT and Topologic Study

Jingwen Zhu, Emilie-Laure Zins, M. Alikhani

► **To cite this version:**

Jingwen Zhu, Emilie-Laure Zins, M. Alikhani. Investigation of Catalytic Dehydrocoupling of Dimethylamine-borane by Titanocene: A DFT and Topologic Study. 11th Triennial Congress of the World Association of Theoretical and Computational Chemistry, Aug 2017, Munich, Germany. hal-03955690

HAL Id: hal-03955690

<https://hal.science/hal-03955690>

Submitted on 25 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Investigation of Catalytic Dehydrocoupling of Dimethylamine-borane by Titanocene: A DFT and Topological Study



Jingwen ZHU, Emilie-Laure ZINS, M. Esmail ALIKHANI
jingwen.zhu@etu.upmc.fr



Laboratoire MONARIS-UMR 8233, Université Pierre et Marie Curie, Sorbonne Universités, 4 Place Jussieu, 75005 Paris, France

Problem position and objectives:

Problem position

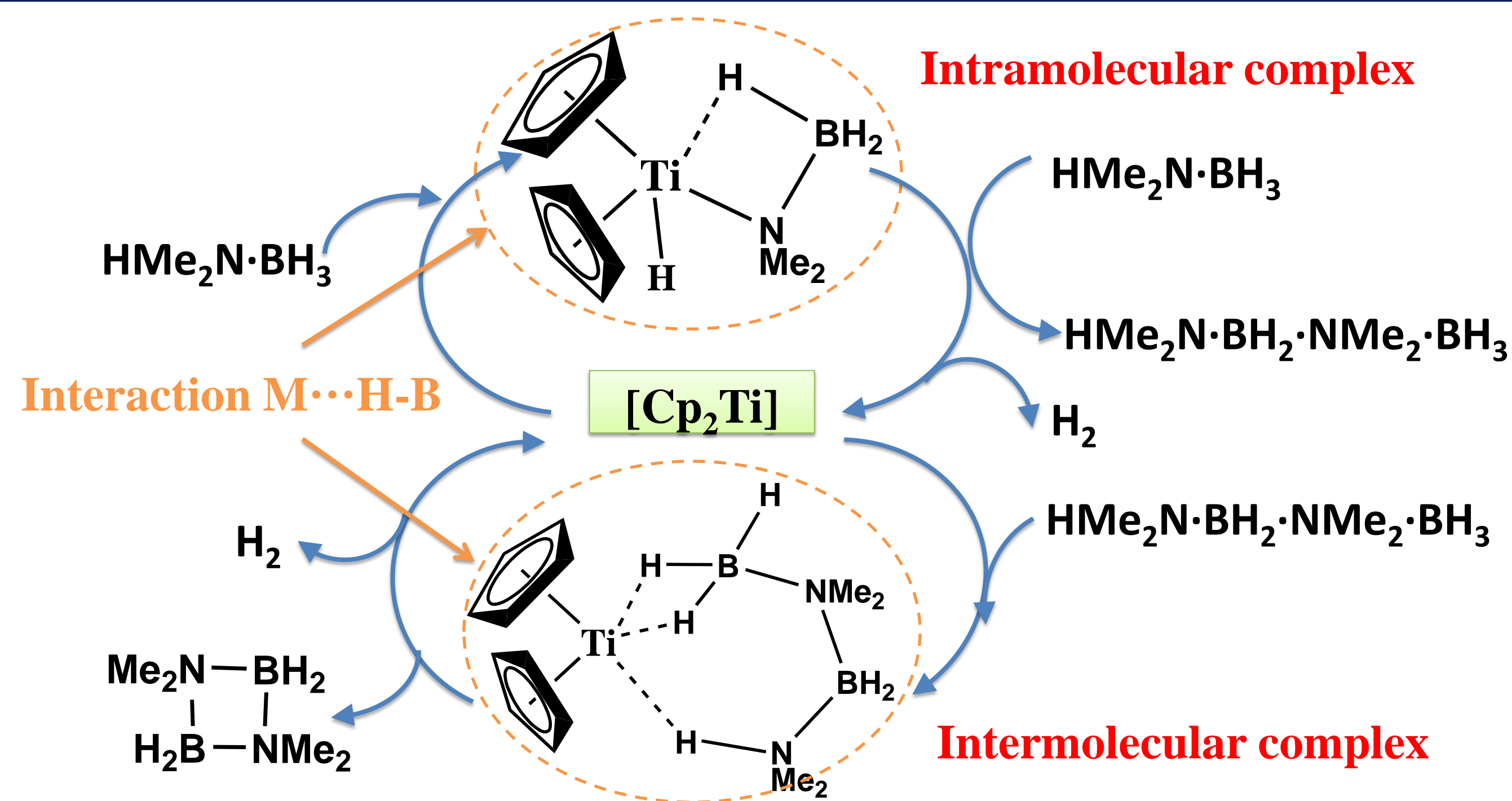
- Increasing demand of clean, efficient and renewable energy carriers => Molecular hydrogen H₂
- Main problems to be solved: sources of H₂ and techniques for hydrogen storage [1]
- Potential hydrogen storage vectors: Catalytic dehydrogenation of ammonia borane and its related amine borane (AB) compounds [2]

Dehydrogenation/dehydrocoupling of amine borane

- Need for inexpensive, environmentally friendly, easily synthesized and stable organometallic catalysts
- Reaction mechanisms still remain uncertain [3][4][5]

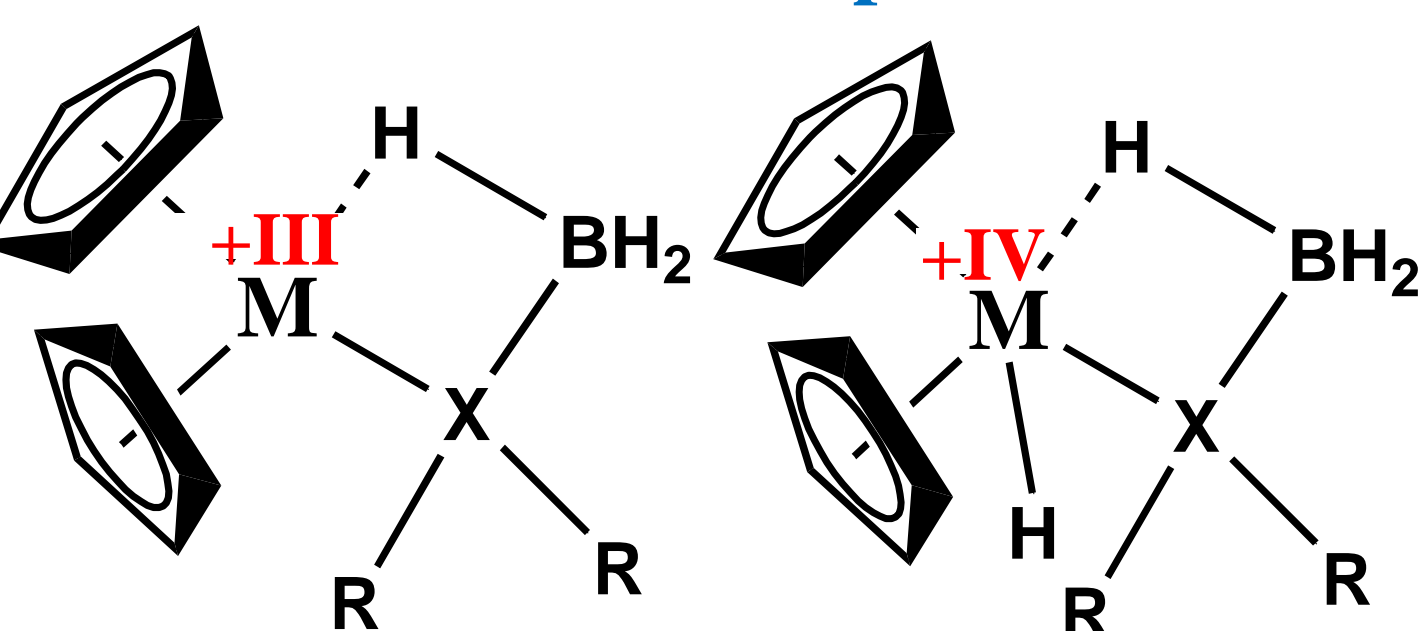
Objectives

- Characterization of 3-centre 2-electron (3C/2e) intermediates with the topological tools: the QTAIM (Quantum Theory of Atoms in Molecules) and the ELF (Electron Localization Function) approach;
- Reinvestigation of different reaction pathways of catalytic dehydrocoupling HMe₂N·BH₃ with the DFT method at molecular level.



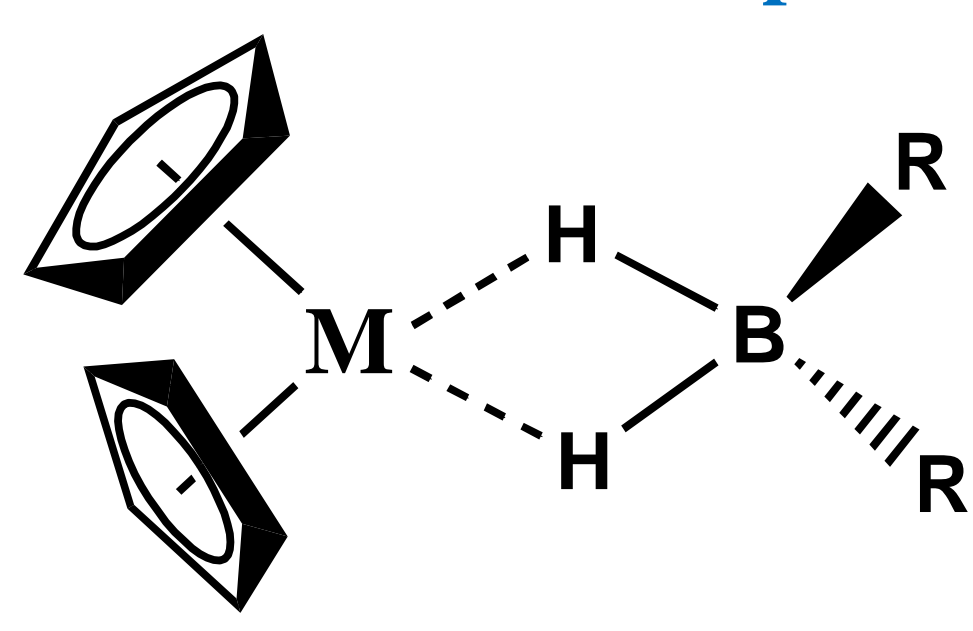
Systematic studies of two families of intermediate

Intramolecular complexes



- M= Ti, Zr and Hf
- X= N (Amine Borane) and P (Phosphine Borane)
- R= H, Me and Ph
- Oxidation state: +III and +IV (E and Z isomers)

Intermolecular complexes



- M = Ti, Zr, V and Nb
- R = Aliphatic, Aromatic, Oxygenated

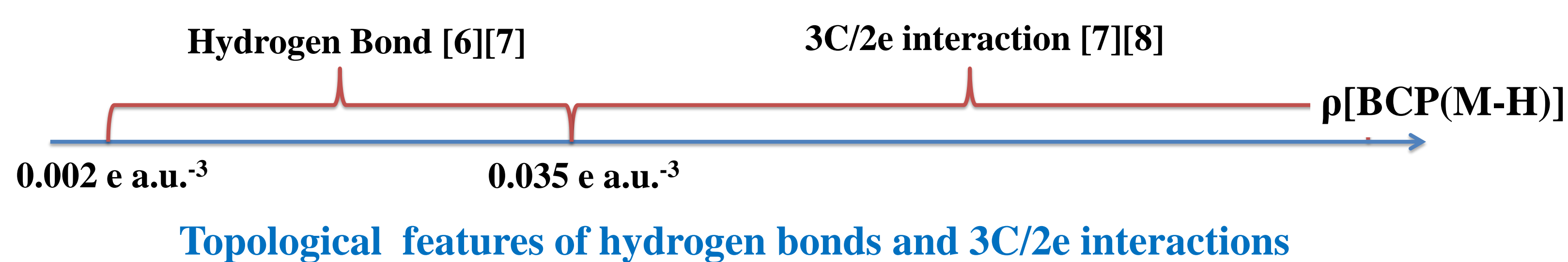
Choice of level of theory

- Weak influence of the exchange-correlation functionals on molecular geometries and electronic (topological) properties
- No influence of the D3-correction on the description of M...H-B interactions
- Importance of relativistic treatment of the metal atom on the description of M...H-B interactions.

- **Geometric optimization:** B3LYP/6-311++G(2d,2p)+LanL2DZ
- **Electronic description:** B3LYP-DKH2 (Second-order Douglas-Kroll-Hess relativistic Hamiltonian)/DZP-DKH

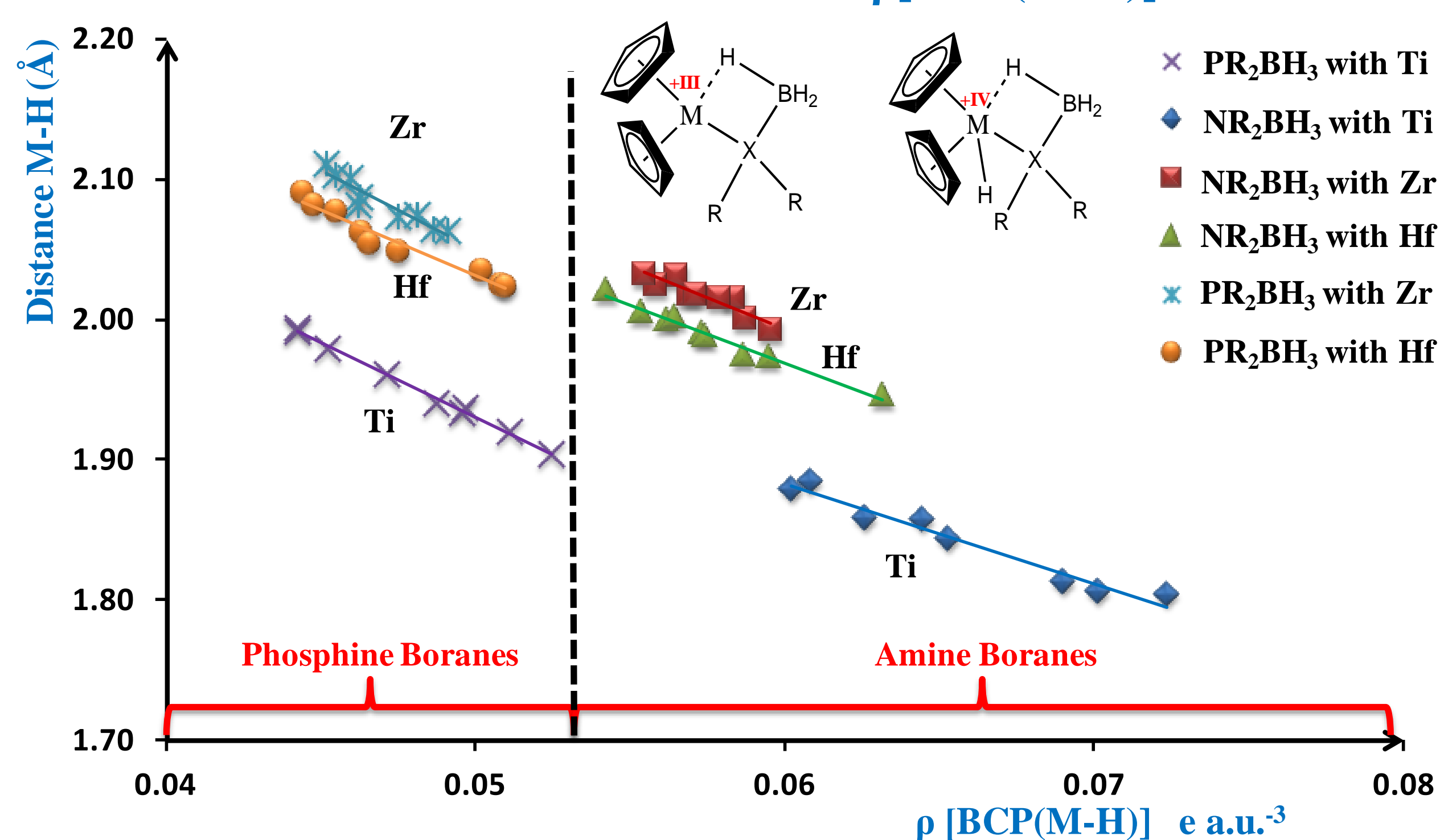
Topological Approaches

		Intramolecular	Intermolecular
QTAIM Analysis	$\rho[\text{BCP}(\text{M}-\text{H})]$	[0.044; 0.072] e a.u. ⁻³	0.049 ~ 0.087 e a.u. ⁻³
	$\nabla^2\rho[\text{BCP}(\text{M}-\text{H})]$	+0.10 ~ +0.17	0.00 ~ +0.16
ELF Analysis	Population of the protonated basin V(H)	1.84 ~ 1.97 e	1.90 ~ 2.08 e
	Atomic contribution of metallic centre C(M)	0.08 ~ 0.13 e	0.05 ~ 0.16 e

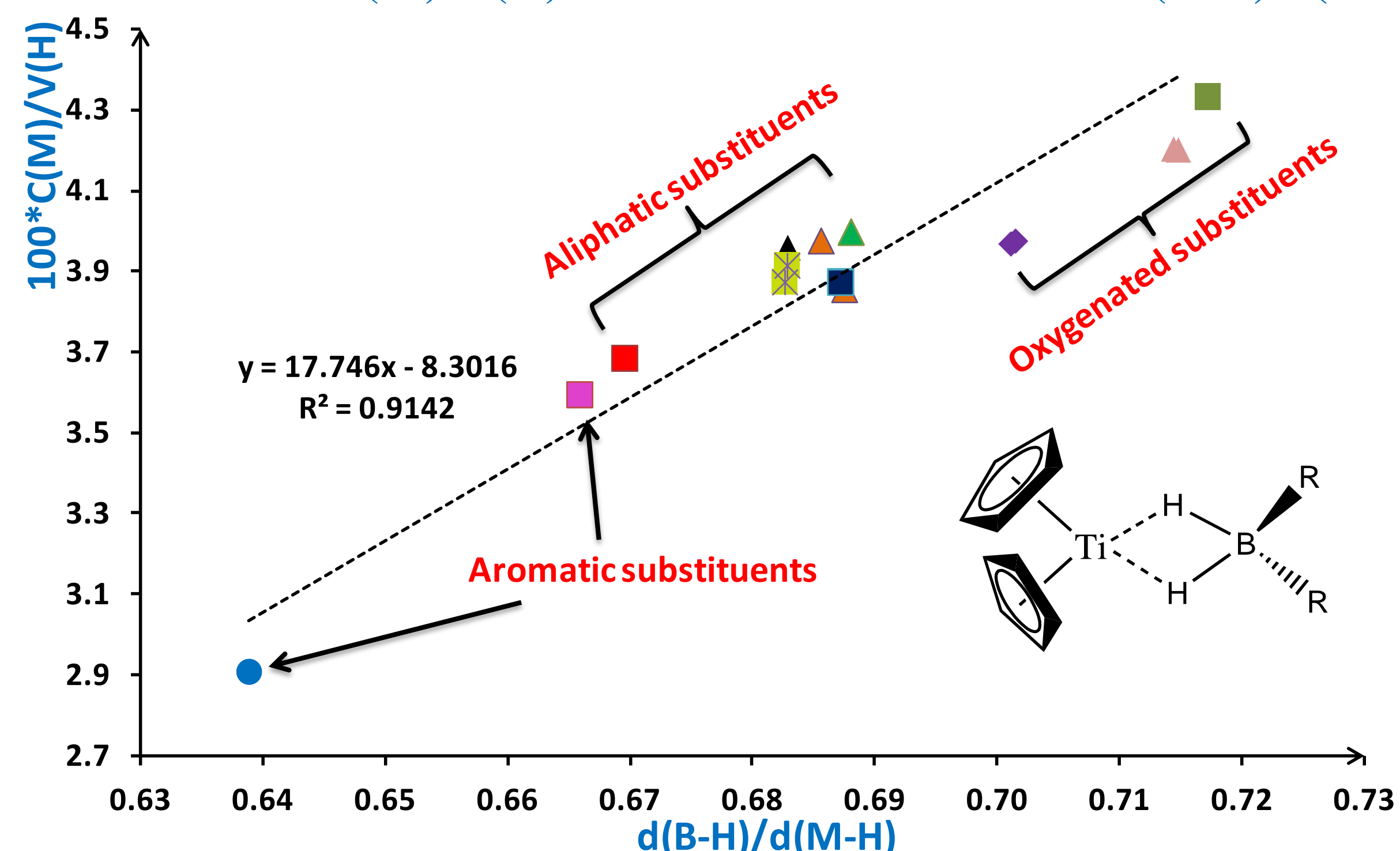


Results and Analysis

Variations of M-H distances with $\rho[\text{BCP}(\text{M}-\text{H})]$



Variations of C(M)/V(H) with the reduced distance $d(\text{B}-\text{H})/d(\text{M}-\text{H})$



Conclusions and Perspectives

- 3C/2e interactions M...H-B are characterized in both intramolecular complexes (agostic complexes) and intermolecular intermediates ones (σ complexes) with the help of DFT methods and the QTAIM and ELF topological approaches.
- Different parameters (nature of metallic centres, ligand and substituent group) may play a significant role for the activation of σ B-H bond.
- Further investigations of catalytic reaction kinetic mechanism will be carried out in considering the empirical correction of dispersion as well as different solvation influences.

References:

- [1] H. C. Johnson, T. N. Hooper and A. S. Weller, *Springer International Publishing* 153 (2015).
- [2] F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.* **25**, 2613 (2007).
- [3] T. J. Clark, C. A. Russell and I. Manners, *J. Am. Chem. Soc.* **128**, 9582 (2006).
- [4] M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.* **132**, 3831 (2010).
- [5] Y. Luo and K. Ohno, *Organometallics* **26**, 3597 (2007).
- [6] U. Koch and P. L. A. Popelier, *J. Phys. Chem.* **99**, 9747 (1995).
- [7] M. Lein, J. A. Harrison and A. J. Nielson, *Dalton. Trans.* **42**, 10939 (2013)
- [8] P. L. A. Popelier and G. Logothetis, *J. Organomet. Chem.* **555**, 101 (1998)