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

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## Problem position and objectives:

### Problem position

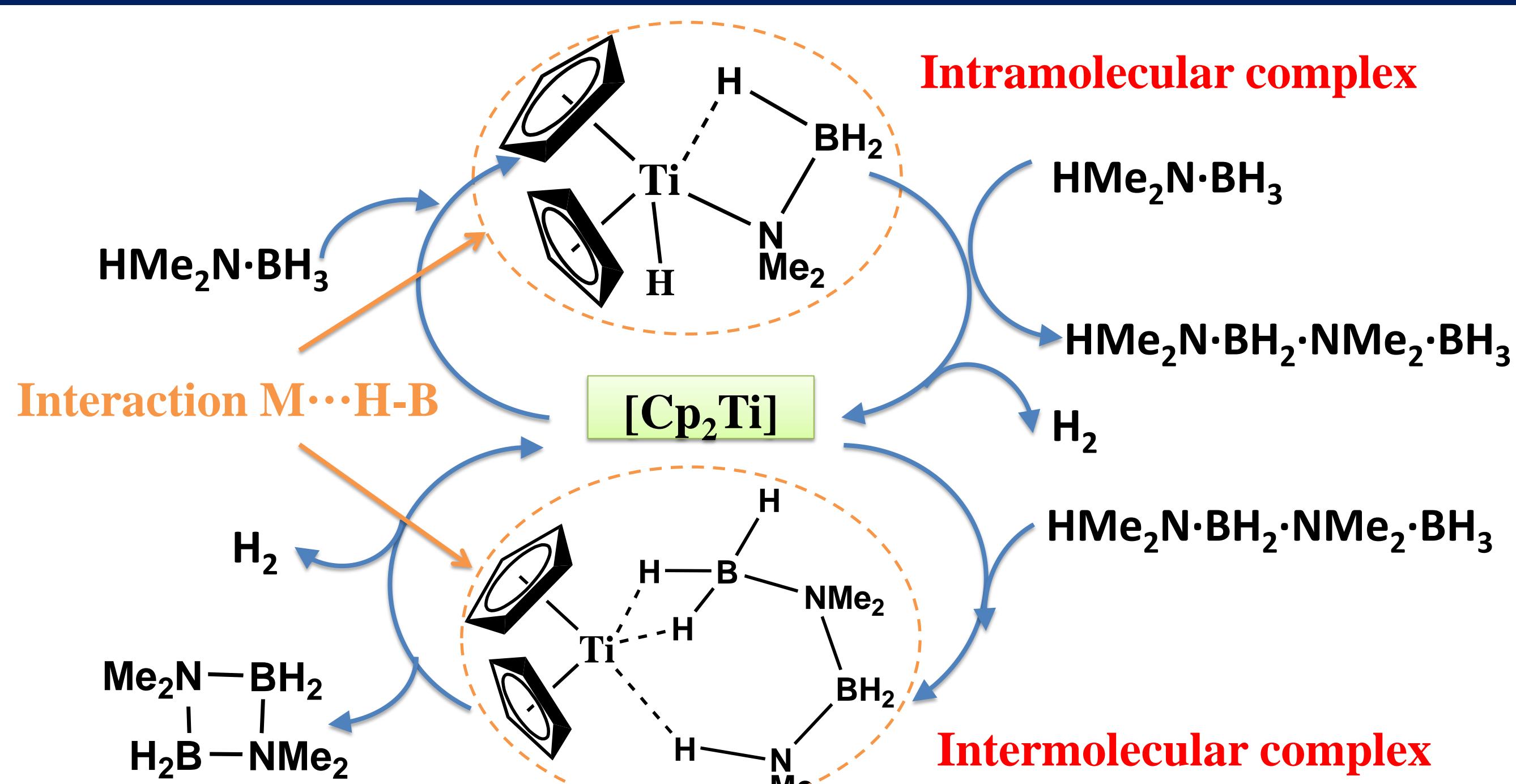
- > Increasing demand of clean, efficient and renewable energy carriers => Molecular hydrogen H<sub>2</sub>
- > Main problems to be solved: sources of H<sub>2</sub> and techniques for hydrogen storage [1]
- > Potential hydrogen storage vectors: Catalytic dehydrogenation of ammonia borane and its related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

### Dehydrogenation/dehydrocoupling of amine borane

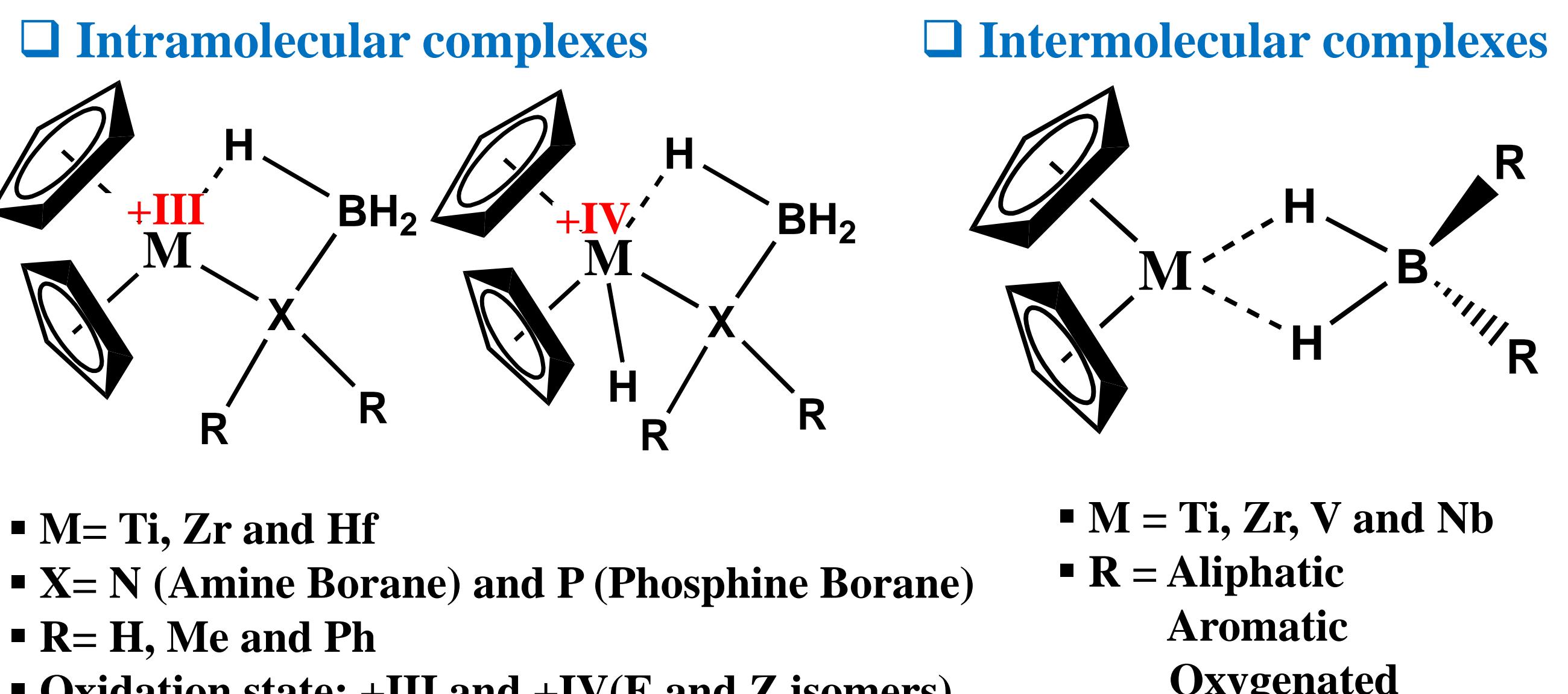
- > Need for inexpensive, environmentally friendly, easily synthesized and stable organometallic catalysts
- > Reaction mechanisms still remain uncertain [3][4][5]

### 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 HMe<sub>2</sub>N·BH<sub>3</sub> with the DFT method at molecular level.



## Systematic studies of two families of intermediate



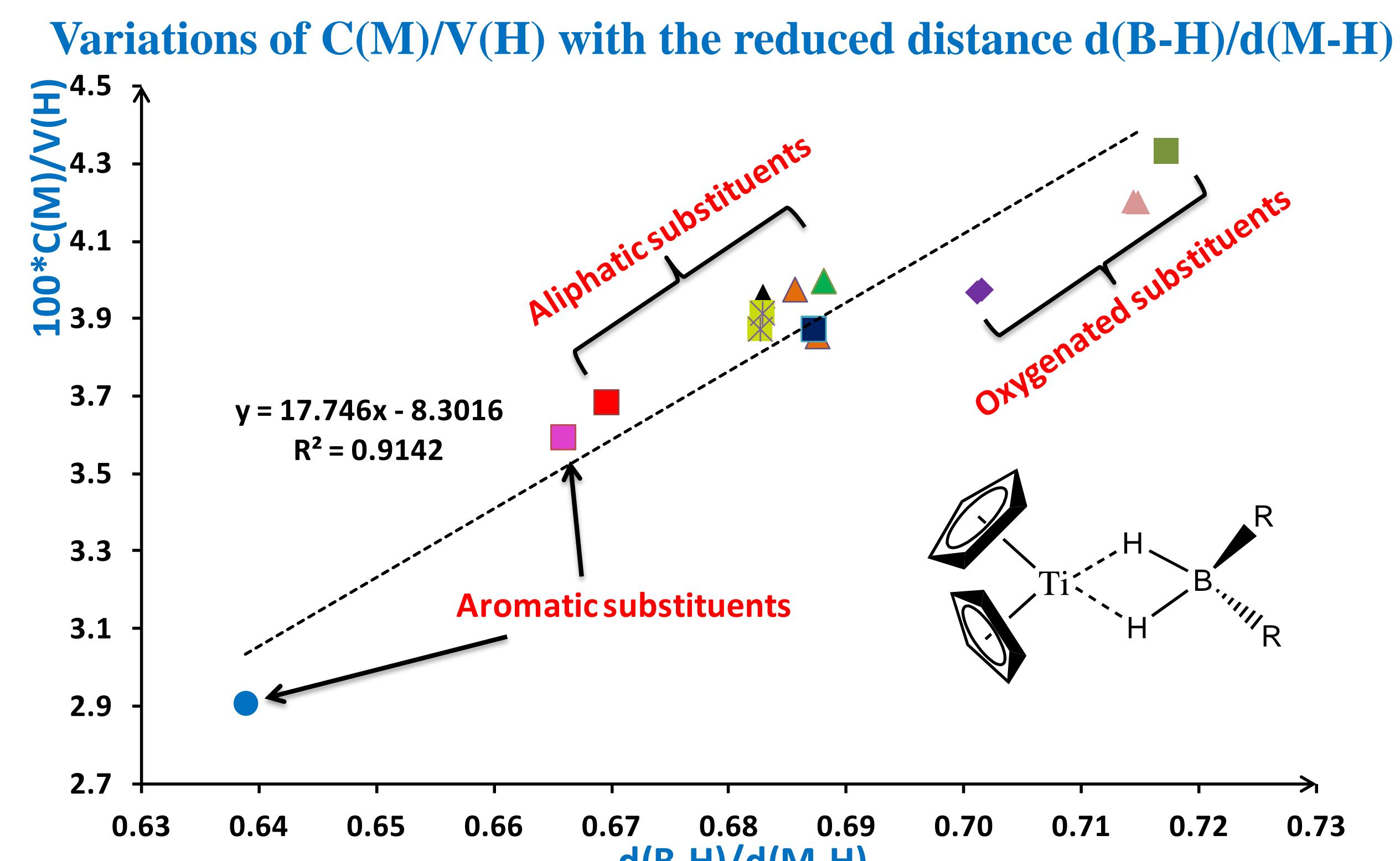
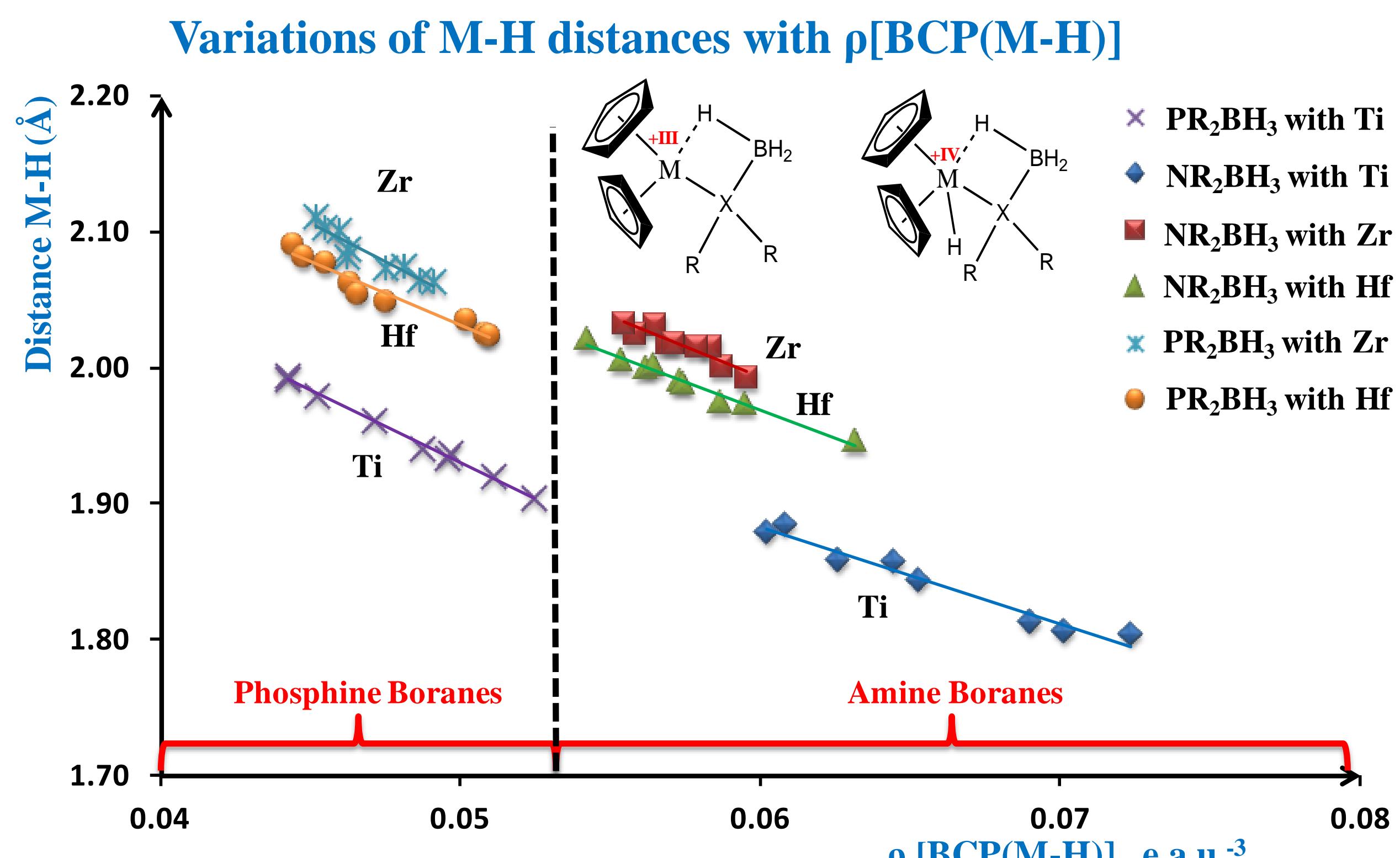
## Choice of level of theory

- 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

	Intramolecular	Intermolecular
QTAIM Analysis	$\rho[\text{BCP}(\text{M}-\text{H})]$ 	[0.044; 0.072] e a.u. <sup>-3</sup> 0.049 ~ 0.087 e a.u. <sup>-3</sup>
	$\nabla^2\rho[\text{BCP}(\text{M}-\text{H})]$	+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
	Hydrogen Bond [6][7] 0.002 e a.u. <sup>-3</sup>	3C/2e interaction [7][8] 0.035 e a.u. <sup>-3</sup>
		$\rho[\text{BCP}(\text{M}-\text{H})]$

Topological features of hydrogen bonds and 3C/2e interactions

## Results and Analysis



## Conclusions and Perspectives

- 3C/2e interactions M···H-B are characterized in both intramolecular complexes (agostic complexes) and intermolecular intermediates ones ( $\sigma$  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  $\sigma$  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.

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