

**NWO/RGC JOINT RESEARCH SCHEME  
COMPLETION REPORT**

**Project Reference Number**

D-HK002/11T

**Project Title**

Metalloradical Activation of Carbon-Carbon Bonds: Combined Experimental and Theoretical Studies  
金屬自由基活化碳碳鍵反應：聯合實驗及理論的研究

**Particulars**

	Hong Kong team				Dutch team
Name of Principal Investigator (with title)	English: Prof. Kin Shing Chan Chinese: 陳建成教授				Prof. Bas de Bruin
Name of Co-Investigator (if any)	English: Chinese:				
Institution or Institutional affiliation	<input type="checkbox"/>	CityU	<input type="checkbox"/>	HKU	Department of Homogeneous Catalysis van 't Hoff Institute for Molecular Sciences Faculty of Science Universiteit van Amsterdam
	<input checked="" type="checkbox"/>	CUHK	<input type="checkbox"/>	HKUST	
	<input type="checkbox"/>	HKBU	<input type="checkbox"/>	LU	
	<input type="checkbox"/>	HKIED	<input type="checkbox"/>	PolyU	
Other project team members (if any)					

**Funding Period**

	1 <sup>st</sup> year	2 <sup>nd</sup> year (if applicable)
Start Date	2011.7.1	2012.7.1
Completion Date	2012.6.30	2013.6.30

**Objective(s) as per original application**

1. To explore, and understand the reactivity of metalloradicals of rhodium(II) porphyrins in C-C bond activation.
2. To gain mechanistic understanding of carbon-carbon bond activation in hydrocarbons by transition metal complexes both experimentally and theoretically.

[Please attach relevant document(s)]

**i) Outline of proposed research and results obtained**

***Fundamental understanding of carbon-carbon bond activation by metalloradical***

Computational theoretical studies by density functional theory by turbomole 6.3.1 (def2-TZVP, b3-lyp, opt) on rhodium(II) porphyrin radical catalyzed rhodium porphyrin hydride insertion into the carbon-carbon bond activation of octane has been performed using the full tetraphenyl porphyrin ligand. The calculated activation parameters are in agreement with the experimental data obtained (at 120 °C and in 15 hours) with  $\Delta H \neq 34.8$  kcal/mole with zero point energy correction and  $\Delta G \neq 48.0$  kcal/mole. Therefore, the mechanism of the key carbon-carbon activation step of cyclooctane by a rhodium(II) porphyrin, a metalloradical, is supported. This provides great insight into the understanding of aliphatic carbon-carbon bond activation by transition metal complex.

**ii) Significance of research results**

***Metalloradical activation of carbon-carbon bond – potential mild alternate energy production method***

Aliphatic carbon-carbon bond activation is an important area of chemical research for the fundamental understanding and application in crude oils degradation (currently at high temperatures over 450 °C and therefore energy intensive) and organic waste treatment for re-utilization as chemicals and fuels. The discovery of metalloradical activation of aliphatic carbon-carbon bond at sufficiently mild temperature of slightly strained cyclic hydrocarbon shed light on the potential of this approach in further hydrogenation of hopefully unstrained carbon-carbon single bond using water as the hydrogenating agent, thus providing an energy attractive method for fuel generation both thermally and upon coupled successfully with sunlight. (See recent first homogenous catalytic hydrogenation using water by rhodium porphyrin: C. T. To, K. S. Choi, K. S. Chan “Catalytic Carbon-Carbon  $\sigma$ -Bond Hydrogenation with Water Catalyzed by Rhodium Porphyrins” *J. Am. Chem. Soc.* **2012**, *134*, 11388-11391.) Furthermore, this carbon-carbon bond can be a new paradigm in organic synthetic method as a direct, catalytic functionalization of hydrocarbons into more values intermediates.

**iii) Research output**

1. Chan, Y. W.; de Bruin, B.; Chan, K. S. "Rhodium(III) Porphyrin Radical Catalyzed Metal Hydride Insertion in Carbon Carbon Bond of Cyclooctane: A Combined Experimental and Theoretical Studies" *Manuscript in preparation*

**iv) Potential for or impact on further research collaboration**

Further computational studies and experimental work on stoichiometric and catalytic carbon-carbon activation especially using water as hydrogenating agent of various hydrocarbons can be explored to gain quantitative understanding of the reaction mechanism.