

RGC Ref.: N_CUHK470/10

NSFC Ref. : 21061160493

(please insert ref. above)

NSFC/RGC Joint Research Scheme
Joint Completion Report

*(Please attach a copy of the completion report submitted to the NSFC
by the Mainland researcher)*

Part A: The Project and Investigator(s)

1. Project Title

Group 4 Metal Complexes for Hydroamination Catalysis

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator <i>(with title)</i>	Professor Zuowei Xie	Professor Yong Tang
Post	Choh-Ming Li Professor of Chemistry	Professor of Chemistry
Unit / Department / Institution	Chemistry/CUHK	Shanghai Institute of Organic Chemistry, CAS
Co-investigator(s) <i>(with title)</i>	NA	NA

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval <i>(must be quoted)</i>
Project Start date	2011-01-01	--	
Project Completion date	2013-12-31	--	
Duration <i>(in month)</i>	36	--	

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_____ to be submitted to the RGC office available.

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

- 1) To design a series of chiral and achiral carborane-, π -cyclic- and phenoxy-amine-based ligands and to prepare and characterize the corresponding group 4 metal complexes.
- 2) To evaluate the catalytic performance of new group 4 metal catalysts in asymmetric/symmetric hydroamination and hydroamination/cyclization reactions.
- 3) To understand catalyst structure/reactivity relationships.

5.2 Revised Objectives

Date of approval from the RGC: _____

Reasons for the change: _____

6. Research Outcome

Major findings and research outcome

(maximum 1 page; please make reference to Part C where necessary)

- (1) Several new multidentate [NOS] and carborane ligands were prepared. The cationic zirconium complex bearing a planar [NOS] ligand is an efficient catalyst for the intramolecular hydroamination of both terminal and internal alkenes with primary and/or secondary amino moiety. Such a catalyst is tolerant to many functional groups. In the presence of a catalytic amount of such complex, tandem intramolecular hydroamination of primary aminodienes proceeds very well, providing an easy access to bicyclic amines. We have also developed a titanacarborane mono-amide catalyzed hydroamination of carbodiimides for the synthesis of mono-/bi-cyclic guanidines in good to excellent yields.

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Chiral guanidines can also be prepared with the retention of the *ee* values from chiral amines (Pub #1, #2 and #9).

- (2) The above-mentioned group 4 metal complexes with [NOS] ligand show high catalytic activity in ethylene polymerization after activation with cocatalyst MAO. The selected resultant polymers with arsine functionality can catalyze Wittig olefination (Pub #4 and #8).
- (3) It was found that reactions of zirconocene-carboryne complex with *N*-heterocycles derived from pyridine gave α -C-H activation products in high yields. These reactions may involve the pyridine coordinated zirconocene-carboryne intermediate. On the other hand, in the absence of group 4 metals, the reactivity patterns of carborynes are very different from those of metal-carboryne complexes. Carborynes undergo [4+2], [2+2] and ene reactions with aromatics, and styrenes (Pub #3, #5-#7 and #11).
- (4) In addition to group 4 metals, a copper catalyzed highly diastereo- and enantioselective cyclopentannulation reaction of indoles with cyclopropanes was also successfully developed. The reaction performed well with a series of indoles and D-A cyclopropanes under mild conditions, giving penta-fused indoline products with excellent diastereoselectivities (up to >50/1 dr) and enantioselectivities (up to 96% *ee*). The application of this reaction to pyrroloindoles established an unprecedented approach to tetracyclic pyrroloindoline compounds (Pub #10).

Research Outcome:

This original work has resulted in 11 peer-reviewed articles published in chemistry journals including J. Am. Chem. Soc. (x 1), Chem. Commun. (x1), Organometallics (x 3), Org. Lett (x 2), Chem. Asian J (x 1), Tetrahedron (x 1), J. Organomet. Chem. (x1) and Acta Chim Sinica (x 1). PI was invited to give two invited lectures at international conferences. Five postgraduate students have been trained.

Potential for further development of the research and the proposed course of action
(*maximum half a page*)

The catalysts developed in this project may also be active in hydrosilylation, hydroboration and hydrophosphination of alkenes and alkynes. We will explore these reactions in the future.

7. The Layman's Summary

(*describe in layman's language the nature, significance and value of the research project, in no more than 200 words*)

Catalytic hydroamination is a highly atom-efficient method for the addition of amines to unsaturated bonds to give new C-N bonds, which has led to intensified research efforts over the last decade as the importance of nitrogen-containing compounds in biological systems and industrially relevant basic and fine chemicals. Various catalyst systems have been developed to achieve this goal. Among them, group 4 metal catalysts are very attractive for their low cost, low toxicity, and high reactivity. However, they are often restricted to certain types of substrates. The development of catalysts for efficient symmetric/asymmetric hydroamination/cyclization of a wide spectrum of substrates is still a great challenge. In this research, we have developed new group 4 metal monoamide [σ : η^1 : η^5 -(OCH₂)(Me₂NCH₂)C₂B₉H₉]Ti(NMe₂) and cationic zirconium alkyl incorporating a

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tridentate [O'N'S] ligand systems to undergo catalytic construction and reconstruction of guanidines via hydroamination process. Asymmetrical hydroamination can be achieved via an elegant design of ligands. A wide range of substrates including both terminal and internal alkenes with primary and/or secondary amino moiety are compatible with these catalytic systems. Such catalysts are also tolerant to many functional groups. The results obtained from this joint efforts offer valuable information on the structure/reactivity relationships and new methodologies for the construction of a variety of N-containing compounds/N-heterocycles in a catalytic manner.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) (<i>bold the authors belonging to the project teams and denote the corresponding author with an asterisk*</i>)	Title and Journal/Book (<i>with the volume, pages and other necessary publishing details specified</i>)	Submitted to RGC (<i>indicate the year ending of the relevant progress report</i>)	Attached to this report (<i>Yes or No</i>)	Acknowledged the support of this Joint Research Scheme (<i>Yes or No</i>)
Publication No.	Year of publication	Under Review	Under Preparation (<i>optional</i>)					
1	2011			Xinke Wang, Zhou Chen, Xiu-Li Sun, Yong Tang,* Zuowei Xie*	Intramolecular Hydroamination of Aminoalkenes Catalyzed by a Cationic Zirconium Complex <i>Org. Lett.</i> 2011 , <i>13</i> , 4758-4761		Yes	Yes
2	2011			Hao Shen, Yang Wang, and Zuowei Xie*	Ti-amide Catalyzed Synthesis of Cyclic Guanidines from Di-/Tri-amines and Carbodiimides," <i>Org. Lett.</i> 2011 , <i>13</i> , 4562-4565		Yes	Yes
3	2011			Shikuo Ren, and Zuowei Xie*	"Reaction of Zirconocene-Carboryne Complex with Pyridines: Ligand C-H Activation," <i>Organometallics</i> 2011 , <i>30</i> , 5953-5959.		Yes	Yes
4	2012			Peng Wang, Chun-Rong Liu, Xiu-Li Sun, Shuai-Shuai Chen, Jun-Fang Li, Zuowei Xie, and Yong Tang*	A newly-designed PE-supported arsine for efficient and practical catalytic Wittig olefination," <i>Chem. Commun.</i> 2012 , 290-292.		Yes	Yes
5	2012			Sunewang Rixin Wang, and Zuowei Xie*	"Reaction of Carboryne with Alkylbenzenes," <i>Organometallics</i> 2012 , <i>31</i> , 3316-3323.		Yes	Yes

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6	2012		Sunewang Rixin Wang, and Zuowei Xie*	"Reaction of Carboryne with Styrene and Its Derivatives," <i>Tetrahedron</i> 2012 , <i>68</i> , 5269-5278.		Yes	Yes
7	2012		Sunewang Rixin Wang, and Zuowei Xie*	"Formal Insertion of <i>o</i> -Carborynes into Ferrocenyl C-H Bond: A Simple Access to <i>o</i> -Carboranylferrocenes," <i>Organometallics</i> 2012 , <i>31</i> , 4544-4550.		Yes	Yes
8	2012		Xinke Wang, Mei-Mei Sit, Jie Sun, Yong Tang* and Zuowei Xie*	"Synthesis, Structure and Ethylene Polymerization Behavior of Group 4 Metal Complexes Bearing Salicylaldaminato Ligands with Appended Donor Functionality," <i>Acta Chim. Sinica</i> 2012 , <i>70</i> , 1909-1916.		Yes	Yes
9	2013		Fangrui Zheng, Jian Zhang, Xiaodu Fu, and Zuowei Xie*	"Reaction of 13-Vertex Carboranes with Strong Base. Synthesis and Structural Characterization of Carborane Monoanions with <i>exo</i> - π -Bonding," <i>Chem. Asian J.</i> 2013 , <i>8</i> , 1886-1891.		Yes	Yes
10	2013		Hu Xiong, Hao Xu, Saihu Liao, Zuowei Xie*, and Yong Tang,*	"Copper-Catalyzed Highly Enantioselective Cyclopentannulation of Indoles with Donor-Acceptor Cyclopropanes," <i>J. Am. Chem. Soc.</i> 2013 , <i>135</i> , 7851-7854.		Yes	Yes
11	2013		Zaozao Qiu, Liang Deng, and Zuowei Xie*	"Reaction of $\text{Li}_2\text{C}_2\text{B}_{10}\text{Me}_8\text{H}_2$ with NiCl_2 . Ligand Effects on Stability of Ni-Octamethylcarboryne Complexes", <i>J Organomet. Chem.</i> 2013 , <i>747</i> , 225-228.		Yes	Yes

9. Recognized International conference(s) in which paper(s) related to this research project was/were delivered (Please attach a copy of each delivered paper)

Month/Year/Place	Title	Conference Name	Submitted to RGC (indicate the year ending of the relevant progress report)	Attached to this report (Yes or No)	Acknowledged the support of this Joint Research Scheme (Yes or No)

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July/2011/ Shanghai	Transition metal mediated C-C coupling between traditional and non-traditional carbon atoms	16 th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis		Yes	Yes
09/2012/ Lisbon	Transition metal mediated functionalization of carboranes	25th International Conference on Organometallic Chemistry		Yes	Yes

10. Student(s) trained (*Please attach a copy of the title page of the thesis.*)

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Xinke Wang	PhD	2006-09-01	2011-10-09
Yang Wang	MPhil	2009-08-01	2011-08-01
Xiaoguang Zhou	PhD	2008-09-01	2013-06-10
Yanshan Gao	PhD	2007-09-01	2012-06-10
Sunewany Rixin Wang	PhD	2009-08-01	2012-07-15

11. Other impact (*e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.*)

Three PhD students have been trained under the co-supervision of both Hong Kong PI and Mainland PI.