

RGC Reference CUHK7/CRF/12G
<i>please insert ref. above</i>

**The Research Grants Council of Hong Kong
Collaborative Research Fund Group Research Projects
Completion Report**
(for completed projects only)

Part A: The Project and Investigator(s)

1. Project Title

Development of New Methodologies for New Carborane Materials

2. Investigator(s) and Academic Department/Units Involved *(please highlight approved changes in the composition of the project team and quote the date when RGC granted approval of such changes)*

Research Team	Name/Post	Unit/Department/Institution	Average number of hours per week spent on this project in the current reporting period
Project Coordinator	Zuowei Xie/ Choh-Ming Li Professor of Chemistry	Chemistry/CUHK	12
Co-Principal investigator(s)	Chi Wu/Wei Lun Professor of Chemistry	Chemistry/CUHK	8
	Guochen Jia/ Chair Professor	Chemistry/HKUST	8
	Zhenyang Lin/Profesor	Chemistry/HKUST	8
	Qian Miao/ Professor	Chemistry/CUHK	8
Collaborators/ Others	NA		

3. Project Duration

	Original	Revised	Date of RGC Approval <i>(must be quoted)</i>
Project Start Date	01/06/2013		
Project Completion Date	31/05/2016		

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Duration (<i>in month</i>)	36		
Deadline for Submission of Completion Report	28/02/2017		

Part B: The Final Report

5. Project Objectives

5.1 Objectives as per original application

1. To understand the similarities and differences in reactivity between traditional M–C bonds involving tetravalent carbon and non-traditional metal–carbon bonds, such as those involving *o*-carborane cages, in which the carbon is six-coordinate

2. To develop transition metal catalyzed/mediated selective C-C and C-B coupling reactions involving carborane cage C or B atoms

3. To understand the reaction mechanisms via combination of experimental and theoretical studies.

4. To utilize the newly developed methodologies for the synthesis of new materials with the functional group carboranes.

5. To explore applications of new functional carboranes as BNCT agents and organic semiconductors.

5.2 Revised objectives

NA

6. Research Outcome

6.1 Major findings and research outcome

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

- (1) The non-classical M–C_{cage} bonds in transition metal-carboranyl complexes are generally inert toward electrophiles, and hence significantly different from traditional M–C bonds involving tetravalent carbon. This can be ascribed to steric effects resulting from the carboranyl moiety. The activation of these M–C_{cage} bonds can be achieved via the formation of metallacycles. On the other hand, the corresponding metal–B_{cage} bond is very reactive toward various unsaturated molecules/electrophiles owing to the highly polarized metal–B bond. These important findings lay a solid ground for the functionalization of cage B–H vertices (Pub #1, #5, #8, #11, and #28).
- (2) A breakthrough has been made in developing transition metal catalyzed carboxylic acid guided selective cage B(4)-monoalkenylation, B(4,5)-dialkenylation, B(4,5)-diarylation and

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B(4)-monoalkynylation, B(4)-hydroxylation, and B(4)-amination. These results indicate that the weakly coordinating –COOH directing group not only plays a key role in regioselectivity and mono-/di-selectivity of the reactions, but also is removable after the reaction. We also isolated the key intermediate bearing five-membered metallacycle MBCCO from the above reaction, which helps us to understand the reaction mechanism. These important findings lay a solid ground for catalytic construction of cage B-(hetero)atom bonds via direct cage B-H activation (Pub #15, #33, #45, and #47).

- (3) Simultaneous cage C,B or cage C,C functionalization of *o*-carboranes has also been succeeded using 1,3-dehydro-*o*-carborane or 1,2-dehydro-*o*-carborane as synthons. The former underwent Diels-Alder reaction with arenes to give [4 + 2] cycloadducts or regioselective aromatic ene reaction to afford cage B-substituted derivatives. The latter underwent α -C–H bond insertion with tertiary amines, affording α -carboranylated amines in very good regioselectivity and isolated yields (Pub #10, #13, #30, #31, #32, #46, #48, #49 and #55).
- (4) Several *o*-carborane functionalized pentacenes were prepared using the method developed in our laboratory. Single-crystal X-ray analyses show that they can form one-dimensional π -stacks. The results show that the incorporation of carboranyl moiety into pentacene core can lower the LUMO energy level by 0.3 eV, converting a typical p-type semiconductor to ambipolar one. In addition, the crystal packing of these molecules can be tuned by the substituents on the second cage carbon. This work clearly indicates that carboranes can serve as electron-deficient building blocks to lower the LUMO energy levels of π -conjugates and to tune the crystal packing, illustrating the unique role of carborane in materials design and development (Pub #34).
- (5) A Rhodamine labeled carborane-functionalized PEG (PEG = polyethyleneglyco) system, 1-S(Rhodamine)-2-S(PEG)-1,2-C₂B₁₀H₁₀ was found to form a liposome-like bi-layer vesicle structure with an average diameter of 200 nm in aqueous solution. It is nontoxic and uptaken easily by cell. This is a new system involving a multifunctional vesicle that can serve as a BNCT (boron neutron capture therapy) agent, a carrier for anti-cancer hydrophilic drugs, and a fluorescent probe for diagnostic imaging, which allows the combination of a BNCT and chemotherapy of cancers in the same treatment (Pub #14).

In summary, this collaborative work has resulted in 60 peer-reviewed articles published in international chemistry journals including JACS (x 7), Angew Chem Int Ed (x 8), Adv. Mater (x 1), Nat. Commun (x 1), Chem. Sci (x 2), and Acc. Chem. Res. (x 1).

Members were invited to give a total of 13 keynote/invited lectures at international or national conferences. 12 postgraduate students were trained, one of them (Dr. ZHAO Da) was awarded the Springer Thesis Award.

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

The developed methodologies constitute a toolbox for the functionalization of *o*-carboranes. Such toolbox can be further expanded. On the other hand, these methodologies can be used to prepare carborane-functionalized materials for applications in various areas. A renewal application is anticipated.

6.3 Research collaboration achieved (*please give details on the achievement and its relevant impact*)

17 out of 60 publications generated from this research are the joint papers among the group members. One PhD student was co-supervised by two group members from CUHK and HKUST, respectively. These joint efforts lead to the better understanding of the reaction mechanisms, the development of new methodology, and the applications of carborane-functionalized molecules in organic semiconductors and biomaterials. Without group efforts, these achievements cannot be realized.

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*)

Carboranes are carbon-boron molecular clusters, which can be viewed as three dimensional analogs to benzene. Their unique characteristics such as thermal and chemical stabilities as well as 3D structures make them attractive building blocks for boron neutron capture therapy agents in medicine, functionalized units in supramolecular design/materials, and versatile ligands in organometallic chemistry. However, there are limited efficient synthetic methods known for the preparation of functional carborane materials because of their unique structure, which has restricted the applications to within a narrow scope. In this research, we have developed several new methods for the selective functionalization of carboranes at the cage carbon or boron vertices. These are (1) transition metal catalyzed direct selective cage BH or CH functionalization, (2) phosphine-catalyzed direct cage CH functionalization, (3) photocatalytic selective functionalization at cage B or C vertices, and (4) efficient and selective functionalization of carboranes via carboryne (1,2-dehydro-o-carboranes or 1,3-dehydro-o-carboranes) or metal-carboryne intermediates. These new methods offer a useful toolbox, allowing us to introduce various functional units to selective sites of the cage. Subsequently, these methods are used to prepare carborane-functionalized molecules for applications in organic semiconductors and biomaterials.

Part C: Research Output**8. Peer-reviewed journal publication(s) arising directly from this research project**

(*Please attach a copy of the 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>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</i>)	Attached to this report (Yes or No)	Acknowledged the support of RGC (Yes or No)	Accessible from the institutional repository (Yes or No)
Year of publication / Publication No	Year of Acceptance	Under Review	Under Preparation (optional)						

	not yet published)					progress report)			
2013 / #1			Zaozao Qiu, Yangjian Quan, and Zuowei Xie*,	Palladium-Catalyzed Selective Fluorination of <i>o</i> -Carboranes, <i>J. Am. Chem. Soc.</i> 2013 , <i>135</i> , 12192-12195.	2014	yes	yes	no	
2013 / #3			Li Xiang, Kazushi Mashima, and Zuowei Xie*	Reaction of [$\eta^1:\eta^5$ -(Me ₂ NCH ₂ CH ₂)C ₂ B ₉ H ₁₀]TaMe ₃ with aryl isocyanides: tantalacborane-mediated facile cleavage of C-N multiple bond, <i>Chem. Commun.</i> 2013 , <i>49</i> , 9039-9041	2014	Yes	yes	no	
2013 / #4			Jian Zhang and Zuowei Xie*	Reaction of 13-Vertex Carborane μ -1,2-(CH ₂) ₄ -1,2-C ₂ B ₁₁ H ₁₁ with Nucleophiles: Linkage Effect on Product Formation, <i>Inorg. Chem.</i> 2013 , <i>52</i> , 10677-10684.	2014	Yes	yes	no	
2013 / #5			Yangjian Quan, Jiji Zhang, and Zuowei Xie*	Three-Component [2+2+1] Cross-Cyclotrimerization of Carboryne, Unactivated Alkene and Trimethylsilylalkyne Co-Mediated by Zr and Ni, <i>J. Am. Chem. Soc.</i> 2013 , <i>135</i> , 18742-18745	2014	Yes	yes	no	
2014 / #6			Zaozao Qiu* and Zuowei Xie*	Generation and Reactivity of <i>o</i> -Carborynes, <i>Dalton Trans.</i> 2014 , <i>43</i> , 4925-4934.	2014	Yes	yes	no	
2014 / #7			Li Xiang and Zuowei Xie*	Conversion of (η^5 -C ₂ B ₉ H ₁₀ R)TaX ₃ (X = Me, NMe ₃) to (η^6 -C ₂ B ₉ H ₁₀ R)TaX' (X' = NMe ₂ , azaallyl) in the absence of reducing agent: synthesis and structure of tantalacboranes incorporating an <i>arachno</i> - η^6 -C ₂ B ₉ ⁴⁻ ligand, <i>Chem. Commun.</i> 2014 , <i>50</i> , 8249-8252	2014	Yes	yes	no	
2014 / #8			Yangjian Quan, Zaozao Qiu, and Zuowei Xie*	Transition Metal Mediated Three-Component Cascade Cyclization: Selective Cage B-C(sp ²) Coupling of Carborane with Aromatics and Synthesis of Carborane-Fused Tricyclics, <i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 7599-7602.	2014	Yes	yes	no	
2014 / #9			Jian Zhang and Zuowei Xie*	Synthesis, Structure, and Reactivity of 13- and 14-Vertex Carboranes, <i>Acc. Chem. Res.</i> 2014 , <i>47</i> , 1623-1633	2014	Yes	yes	no	
2014 / #10			Da Zhao, Jiji Zhang, and Zuowei Xie*	1,3-Dehydro- <i>o</i> -Carborane: Generation and Reaction with Arenes, <i>Angew. Chem. Int. Ed.</i> 2014 , <i>53</i> , 8488-8491	2014	Yes	yes	no	
2014 /			Jiji Zhang, Yangjian Quan,	Insight into Reaction Mechanism of	2014	yes	yes	no	

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#11			Zhenyang Lin,* and Zuowei Xie*	[2+2+1] Cross-Cyclootrimerization of Carboryne with Alkene and Trimethylsilylaryllalkyne Mediated by Nickel Complex, <i>Organometallics</i> 2014 , <i>33</i> , 3556-3563.				
2014 / #12			Jian Zhang and Zuowei Xie*	On Desilylation of 13-Vertex Carborane 1,2-Me ₂ Si(CH ₂) ₂ -1,2-C ₂ B ₁₁ H ₁₁ , <i>Chin. J. Chem.</i> 2014 , <i>32</i> , 777-782	2014	Yes	yes	no
2014 / #13			Da Zhao, Jiji Zhang, and Zuowei Xie*	Regioselective Insertion of <i>o</i> -Carborynes into α -C-H Bond of Tertiary Amines: Synthesis of α -Carboranylated Amines, <i>Angew. Chem. Int. Ed.</i> 2014 , <i>53</i> , 12902-12906	2014	Yes	yes	no
2014 / #14			Gaojian Chen, Jingying Yang, Gang Lu, Pi Chu Liu, Qianjin Chen, Zuowei Xie, and Chi Wu*	One Stone Kills Three Birds: Novel Boron-Containing Vesicles for Potential BNCT, Controlled Drug Release, and Diagnostic Imaging, <i>Mol. Pharmaceutics</i> 2014 , <i>11</i> , 3291-3299.	2014	Yes	yes	no
2014 / #15			Yangjian Quan and Zuowei Xie*	Iridium Catalyzed Regioselective Cage Boron Alkenylation of <i>o</i> -Carboranes via Direct Cage B-H Activation, <i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 15513-15516.	2014	Yes	yes	no
2014 / #16			Lian-Wei Li,* Xu Wang, Jinxian Yang, Xiaodong Ye,* Chi Wu	Degradation Kinetics of Model Hyperbranched Chains with Uniform Subchains and Controlled Locations of Cleavable Disulfide Linkages, <i>Macromolecules</i> , 2014 , <i>47</i> , 650-658.	2014	Yes	yes	no
2014 / #17			Yonggang Shangguan,* Dameng Guo, Hui Feng, Yuan Li, Xiangjun Gong, Qianjin Chen, Bo Zheng,* and Chi Wu*	Mapping Phase Diagrams of Polymer Solutions by a Combination of Micro-fluidic Solution Droplets and Laser Light-Scattering Detection, <i>Macromolecules</i> , 2014 , <i>47</i> , 2496-2502	2014	Yes	yes	No
2014 / #18			Xu Wang, Lianwei Li, Xiaodong Ye* and Chi Wu	Comparative Study of Solution Properties of Amphiphilic 8-shaped Cyclic-(Polystyrene- <i>b</i> -Polyacrylic Acid) ₂ and Its Linear Precursor, <i>Macromolecules</i> , 2014 , <i>47</i> , 2487-2495	2014	Yes	yes	no
2014 / #19			Yongzhen Ma*, Chi Wu	Revisit Complexation Between DNA and Polyethylenimine When and Where -S-S- linked PEI Is Cleaved Inside the Cell, <i>Journal of Materials Chemistry B.</i> , 2014 , <i>2</i> , 3282-3291	2014	Yes	yes	No
2014 / #20			Hiroki Asakawa, Ka Ho Lee, Zhenyang Lin,* Makoto Yamashita*	Facile Scission of Isonitrile C N Triple Bond Using A Diborane(4) Reagent, <i>Nature Communications</i> , 2014 , <i>5</i> , 4245-4253	2014	Yes	Yes	No
2014 / #21			Wen-Jie Chen and Zhenyang Lin*	DFT studies on the mechanism of palladium-catalyzed carbon-silicon cleavage for the synthesis of benzosilole derivatives, <i>Dalton</i>	2014	yes	Yes	No

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				<i>Trans.</i> , 2014 , <i>43</i> , 11138-11144				
2014 / #22			Wei Bai, Sunny Kai San Tse, Ka Ho Lee, Herman H. Y. Sung, Ian D. Williams,* Zhenyang Lin,*Guochen Jia*	Synthesis and characterization of MH ··HOR dihydrogen bonded ruthenium and osmium complexes ($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH}$)MH(PPh ₃) ₂ (M = Ru, Os), <i>Sci China Chem</i> , 2014 , <i>57</i> , 1079–1089.	2014	Yes	yes	No
2014 / #23			Ran Lin, Ka-Ho Lee, Ka Chun Poon, Herman H. Y. Sung, Ian D. Williams,* Zhenyang Lin,* and Guochen Jia*	Synthesis of Rhenabenzenes from the Reactions of Rhenacyclobutadienes with Ethoxyethyne, <i>Chem. Eur. J.</i> 2014 , <i>20</i> , 14885 – 14899.	2014	Yes	yes	No
2014 / #24			Danqing Liu, Zikai He, Yaorong Su, Ying Diao, Stefan C. B. Mannsfeld, Zhenan Bao, Jianbin Xu, Qian Miao*	Self-Assembled Monolayers of Cyclohexyl-Terminated Phosphonic Acids as a General Dielectric Surface for High-Performance Organic Thin-Film Transistors, <i>Advanced Materials</i> , 2014 , <i>26</i> , 7190-7196.	2014	Yes	yes	No
2015 / #25			Jiji Zhang, Xiaodu Fu, Zhenyang Lin* and Zuowei Xie*	Supercarborane Radical Anions w“Supercarborane Radical Anions with [2n + 3] Electron Counts: A Combined Experimental and Theoretical Study, <i>Inorg. Chem.</i> 2015 , <i>54</i> , 1965-1973. 2015 , <i>54</i> , 1965-1973.	no	yes	yes	No
2015 / #26			Fangrui Zheng and Zuowei Xie*,	Reaction of <i>N</i> -Heterocyclic Carbenes with 13-Vertex <i>closo</i> -Carboranes: Synthesis and Structural Characterization of Zwitterionic Salts of 13-Vertex <i>nido</i> -Carboranes, <i>Org. Chem. Front.</i> 2015 , <i>2</i> , 55-59.	No	yes	yes	No
2015 / #27			Jingying Yang and Zuowei Xie*	Synthesis, Structure and Reactivity of Rare-Earth Metallocarborane Alkyls [$\eta^1:\eta^5\text{-O}(\text{CH}_2)_2\text{C}_2\text{B}_9\text{H}_9$]Ln($\sigma:\eta^1\text{-CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$)(THF) ₂ , <i>Dalton Trans.</i> 2015 , <i>44</i> , 6630-6637.	No	yes	yes	No
2015 / #28			Yangjian Quan and Zuowei Xie*	Palladium-Catalyzed Regioselective Intramolecular Coupling of <i>o</i> -Carborane with Aromatics via Direct Cage B–H Activation,” <i>J. Am. Chem. Soc.</i> 2015 , <i>137</i> , 3502-3505.	No	yes	yes	no
2015 / #29			Jingying Yang and Zuowei Xie*	Reactivity of Traditional Metal–Carbon (alkyl) versus Nontraditional Metal–Carbon (cage) Bonds in Organo-Rare-Earth Metal Complexes [$\eta^5\text{-}\sigma\text{-}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})$]Ln(CH ₂ C ₆ H ₄ - <i>o</i> -NMe ₂)(THF) ₂ , <i>Organometallics</i> 2015 , <i>34</i> , 2494-2499.	No	yes	yes	No
2015 / #30			Cen Tang and Zuowei Xie*	Nickel Catalyzed Cross-Coupling Reactions of <i>o</i> -Carboranyl with Aryl Iodides: Facile Synthesis of 1-Aryl- <i>o</i> -Carboranes and 1,2-Diaryl- <i>o</i> -Carboranes, <i>Angew. Chem. Int. Ed.</i> 2015 , <i>54</i> , 7662-7665.	No	yes	yes	no
2015 /			Da Zhao, Jiji Zhang and	Facial Synthesis of	no	yes	yes	no

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#31			Zuwei Xie*	<i>o</i> -Carborane-Substituted Alkenes and Allenes via Regioselective Ene Reaction of 1,3-Dehydro- <i>o</i> -Carborane, <i>Chem. Eur. J.</i> 2015, 21, 10334-10337				
2015 / #32			Da Zhao, Jiji Zhang and Zuwei Xie*	Dearomatic [2+2] Cycloaddition and Formal C–H Insertion Reaction of <i>o</i> -Carboryne with Indoles: Synthesis of Carborane-Functionalized Heterocycles, <i>J. Am. Chem. Soc.</i> 2015, 137, 9423-9428.	No	yes	yes	no
2015 / #33			Hairong Lyu, Yangjian Quan and Zuwei Xie*	Palladium Catalyzed Direct Dialkenylation of Cage B–H Bonds in <i>o</i> -Carboranes Through Cross-Coupling Reaction,” <i>Angew. Chem. Int. Ed.</i> 2015, 54, 10623-10626.	No	yes	yes	no
2015 / #34			Jixi Guo, Danqing Liu, Jiahui Zhang, Jiji Zhang, Qian Miao* and Zuwei Xie*	<i>o</i> -Carborane functionalized pentacenes: synthesis, molecular packing and ambipolar organic thin-film transistors, <i>Chem. Commun.</i> 2015, 51, 12004-12007.	No	yes	yes	No
2015 / #35			Hao Wang, Jiji Zhang, Zhenyang Lin* and Zuwei Xie*	The Synthesis and Structure of a Carbene-Stabilized Iminocarboranylboron(I) Compound, <i>Chem. Commun.</i> 2015, 51, 16817-16820.	No	yes	yes	No
2015 / #36			Jiji Zhang, Zhenyang Lin* and Zuwei Xie*	“DFT Studies on Structures, Stabilities, and Electron Affinities of <i>closo</i> -Supercarboranes C ₂ B _n 2H _n (n = 13 – 20),” <i>Organometallics</i> 2015, 34, 5576-5588.	No	yes	yes	No
2015 / #37			Zhuojun Dai,* Yinglan Shu, Chao Wan, and Chi Wu	Effects of pH and thermally sensitive hybrid gels on osteogenic differentiation of mesenchymal stem cells, <i>J. Biomater. Appl.</i> 2015, 29, 1272-1283.	No	yes	yes	No
2015 / #38			Xu Wang,* Lianwei Li, Weidong He, and Chi Wu*	Formation of Hyperbranched Amphiphilic Terpolymers and Unimolecular Micelles in One-Pot Copolymerization, <i>Macromolecules</i> 2015, 48, 7327-7334.	No	yes	yes	no
2015 / #39			Hiroki Asakawa, Ka-Ho Lee, Ko Furukawa,* Zhenyang Lin,* and Makoto Yamashita*	Lowering the Reduction Potential of a Boron Compound by Means of the Substituent Effect of the Boryl Group: One-Electron Reduction of an Unsymmetrical Diborane(4), <i>Chem. Eur. J.</i> 2015, 21, 4267 – 4271.	No	yes	yes	No
2015 / #40			Man Sing Cheung, Fu Kit Sheong, Todd B. Marder,* and Zhenyang Lin*	Computational Insight into Nickel-Catalyzed Carbon–Carbon versus Carbon–Boron Coupling Reactions of Primary, Secondary, and Tertiary Alkyl Bromides, <i>Chem. Eur. J.</i> 2015, 21, 7480 – 7488.	No	yes	yes	No
2015 /			Wei Bai, Guochen Jia*	Ruthenium-catalyzed b-alkylation of	no	yes	yes	No

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#41				secondary alcohols with primary Alcohols, <i>Inorg. Chimica Acta</i> 2015, 431, 234–241.				
2015 / #42			Ran Lin, Ka-Ho Lee, Herman H. Y. Sung, Ian D. Williams,* Zhenyang Lin,* and Guochen Jia*	Rhenabenzenes and Unexpected Coupling Products from the Reactions of Rhenacyclobutadienes with Ethoxyethyne, <i>Organometallics</i> 2015, 34, 167–176	No	yes	yes	No
2015 / #43			Jiangxi Chen, Ka-Ho Lee, Tingbin Wen, Feng Gao, Herman H. Y. Sung, Ian D. Williams,* Zhenyang Lin,* and Guochen Jia*	Rearrangement of Metallabenzynes to Chlorocyclopentadienyl Complexes, <i>Organometallics</i> 2015, 34, 890–896.	No	yes	yes	No
2015 / #44			Wei Bai, Ka-Ho Lee, Sunny Kai San Tse, Ka Wing Chan, Zhenyang Lin,* and Guochen Jia*	Ruthenium-Catalyzed Deuteration of Alcohols with Deuterium Oxide, <i>Organometallics</i> 2015, 34, 3686–3698.	No	yes	yes	No
2016 / #45			Yangjian Quan and Zuowei Xie*	Palladium-Catalyzed Regioselective Diarylation of <i>o</i> -Carboranes via Direct Cage B-H Activation, <i>Angew. Chem. Int. Ed.</i> 2016, 55, 1295-1298.	No	yes	yes	No
2016 / #46			Da Zhao and Zuowei Xie*	Visible-Light-Promoted Photocatalytic B-C Coupling via Boron-Centered Carboranyl Radical: Facile Synthesis of B(3)-Arylated <i>o</i> -Carboranes, <i>Angew. Chem. Int. Ed.</i> 2016, 55, 3166-3170	No	yes	yes	No
2016 / #47			Yangjian Quan, Cen Tang and Zuowei Xie*	Palladium Catalyzed Regioselective B-C(sp) Coupling via Direct Cage B-H Activation: Synthesis of B(4)-Alkynylated <i>o</i> -Carboranes, <i>Chem. Sci.</i> 2016 , 7, 5838-5845.	No	yes	yes	No
2016 / #48			Da Zhao and Zuowei Xie*	[3-N ₂ - <i>o</i> -C ₂ B ₁₀ H ₁₁][BF ₄]: A Useful Synthone for Multiple Cage Boron Functionalization of <i>o</i> -Carborane, <i>Chem. Sci.</i> 2016 , 7, 5635-5639.	No	yes	yes	No
2016 / #49			Da Zhao and Zuowei Xie*	Recent Advances in the Chemistry of Carborynes, <i>Coord. Chem Rev.</i> 2016, 314, 14-33	No	yes	yes	No
2016 / #50			Jinge Cai,* Yanan Yue, Yanjing Wang, Zhenyu Jin, Fan Jin, Chi Wu*	Quantitative Study of Effects of Free Cationic Chains on Gene Transfection in Different Intracellular Stages, <i>Journal of Controlled Release</i> , <i>Journal of Controlled Release</i> , 2016, 238, 71-79.	No	yes	yes	No
2016 / #51			Zhuojun Dai,* Yinglan Shu, Chao Wan,* Chi Wu	Effects of Culture Substrate Made of Poly(N-Isopropylacrylamide-Co-Acrylic Acid) Microgels on Osteogenic Differentiation of Mesenchymal Stem Cells, <i>Molecules</i> , 2016, 21, 1192	No	yes	yes	No
2016 / #52			Jianqi Wang, Chi Wu*	Reexamination of the Origin of Slow Relaxation in Semidilute Polymer Solutions---Reptation Related or Not?, <i>Macromolecules</i> , 2016, 49, 3184-3191.	No	yes	yes	No

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2016 / #53			Chiemi Kojima, Ka-Ho Lee, Zhenyang Lin,* Makoto Yamashita*	Direct and Base-Catalyzed Diboration of Alkynes with Unsymmetrical Diborane(4), pinB-BMes ₂ , <i>J. Amer. Chem. Soc.</i> , 2016 , <i>138</i> , 6662-6669	No	Yes	yes	No
2016 / #54			Takuto Ohsato, Yuri Okuno, Shintaro Ishida, Takeaki Iwamoto, Ka-Ho Lee, Zhenyang Lin,* Makoto Yamashita,* Kyoko Nozaki*	A Potassium Diboryllithate: Synthesis, Bonding Properties, and the Deprotonation of Benzene, <i>Angew. Chem. Int. Ed.</i> , 2016 , <i>55</i> , 11426-11430	No	Yes	Yes	no
2016 / #55			Fangrui Zheng, Tsz-Fai Leung, Ka-Wing Chan, Herman H. Y. Sung; Williams, Ian D. Williams, Zuowei Xie*, Guochen Jia*	Phosphine-catalyzed cage carbon functionalization of o-carborane: facile synthesis of alkenylcarboranes, <i>Chem. Commun.</i> 2016 , 10767-10770	No	Yes	yes	No
2016 / #56			Ting Bin Wen, Ka-Ho Lee, Jiangxi Chen, Wai Yiu Hung, Wei Bai, Huacheng Li, Herman H. Y. Sung, Ian D. Williams, Zhenyang Lin,* and Guochen Jia*	Preparation of Osmium η^3 -Allenylcarbene Complexes and Their Uses for the Syntheses of Osmabenzynes Complexes, <i>Organometallics</i> , 2016 , <i>35</i> , 1514-1525	No	Yes	Yes	No
2016 / #57			Ka Wing Chan, Wei Bai, Kui Fun Lee, Ka-Ho Lee, Herman H. Y. Sung, Ian D. Williams, Zhenyang Lin,* and Guochen Jia*	Synthesis of Rhenium Vinylidene and Carbyne Complexes from Reactions of [Re(dppm) ₃]I with Terminal Alkynes and Alkynols, <i>Organometallics</i> , 2016 , <i>35</i> , 3520- 3529	No	Yes	yes	no
2016 / #58			Wei Bai, Ka-Ho Lee, Herman H. Y.;Sung, Ian D. Williams,* Zhenyang Lin,* and Guochen Jia*	Alkyne Metathesis Reactions of Rhenium(V) Carbyne Complexes, <i>Organometallics</i> 2016 , <i>35</i> , 3808-3815	No	Yes	yes	No
2016 / #59			Jiangxi Chen, Ka-Ho Lee, Herman H. Y.; Sung, Ian D. Williams,* Zhenyang Lin,* and Guochen Jia*	Synthesis and characterization of dirhenadehydro[12]annulenes <i>Angew. Chem. Int. Ed.</i> 2016 , <i>55</i> , 7194-7198.	No	Yes	yes	No
2017 / #60			Wei Bai, Ka-Ho Lee, Wai Yiu Hung, Herman H. Y. Sung, Ian D. Williams, Zhenyang Lin,* and Guochen Jia*	Reactions of Osmium Carbyne Complexes OsCl ₃ (\equiv CR)(PPh ₃) ₂ (R = CH=CPh ₂ , CH ₂ Ar) with Bromine and Hydrogen Peroxide, <i>Organometallics</i> 2017 , <i>36</i> , in press.	No	Yes	yes	No
2017 / #61			Jianqi Wang,* Fengjie Zhang, Wing Pui Tsang, Chao Wan,* Chi Wu	Fabrication of Injectable High Strength Hydrogel Based on 4-Arm Star Peg for Cartilage Tissue Engineering, <i>Biomaterials</i> , 2017 , <i>120</i> , 11-21.	No	yes	yes	No

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

Month/Year/ Place / No	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 RGC (Yes or No)	Accessible from the institutional repository (Yes or No)
8/2013/Singapore / #1	Metal—carboryne complexes and their role in functionalization of carboranes	15th Asian Chemical Congress	2014	yes	yes	no
11/2013/Jeju / #2	Reactivity of non-traditional metal-carbon bonds: functionalization of carboranes	The 4th Asian Conference on Coordination Chemistry	2014	Yes	yes	No
7/2013/Beijing / #3	非经典金属-碳键和烯及炔的反应: 碳硼烷的官能团化	The 7th National Conference on Coordination Chemistry	2014	Yes	yes	No
7/2014/Singapore / #4	Transition metal mediated multi-component cross coupling reactions of carboryne, alkene and alkyne	The 41st International Conference on Coordination Chemistry	2014	Yes	yes	No
7/2014/Sapporo / #5	Transition metal mediated three-component cross-cyclotrimerization of Carboryne, alkene and alkyne	The 26th International Conference on Organometallic Chemistry	2014	Yes	yes	No
6/2014/Newark / #6	Functionalization of carboranes via transition metal mediated three-component cross-cyclotrimerization	XIV Boron in the Americas Conference	2014	Yes	yes	No
8/2014/Lanzhou / #7	Transition Metal Mediated C-H/B-H Functionalization of Carboranes	The 18th National Conference on Organometallic Chemistry	2014	Yes	yes	No
4/2014/Warwick, UK / #8	Boryl Ligands and Their Roles in Metal-Catalyzed Borylation Reactions	Dalton 2014	2014	Yes	Yes	No
12/2015/Hawaii, USA/#9	Computational insight into nickel-catalyzed carbon-carbon vs. carbon-boron coupling reactions of primary, secondary, and tertiary alkyl bromides	The International Chemical Congress of Pacific Basin Societies 2015	no	Yes	Yes	No
06/2015/Caen, France/#10	Reactivity of 1,2-dehydro-o-carborane: synthesis of substituted o-carboranes	11th International Conference on Heteroatom Chemistry (ICHAC-11)	No	Yes	Yes	No
07/2015/Hong Kong/#11	Transition Metal Catalyzed Functionalization of Carboranes	5th Asian Coordination Chemistry Conference (ACCC-5)	No	Yes	Yes	No

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12/2015/Hawaii, USA/#12	Transition Metal Catalyzed Functionalization of Carboranes via B-H Activation	The International Chemical Congress of Pacific Basin Societies 2015	No	Yes	Yes	No
10/2016/Beijing, China/#13	Computational insight into nickel-catalyzed carbon-carbon vs. carbon-boron coupling reactions of primary, secondary, and tertiary alkyl bromides	International Symposium Of Computational Organometallic Catalysis	No	Yes	Yes	NO
8/2015/Beijing, China/#14	Molecular Assemblies in High-Performance Organic Thin Film Transistors	The 10th National Symposium on Electronic Process in Organic Solids	No	Yes	Yes	NO
7/2016/Dalian, China/#15	Recent Progress of n-channel Organic Thin Film Transistors	30th Annual Meeting of Chinese Chemical Society	No	Yes	Yes	NO

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
Wenjun Xu	MPhil	1/8/2012	29/9/2014
Hao Wang	Ph.D	1/8/2011	15/11/2015
Yangjiang Quan	Ph.D	1/8/2011	20/7/2015
Fan Ting	PhD	1/9/2010	31/8/2014
Wei Bai	Ph.D.	1/2/2012	31/1/2016
Danqing Liu	PhD	1/8/2010	31/07/2014
Lee Ka Ho	PhD	1/9/2011	31/8/2015
Ka Wing Chan	MPhil	1/9/2013	31/7/2015
Jiji Zhang	PhD	1/8/2011	30/9/2015
Da Zhao	PhD	1/8/2011	15/7/2015
Cen Tang	PhD	1/8/2012	1/7/2017
Sheong Fu Kit	PhD	1/9/2012	31/8/2016

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

We have developed close collaboration with Prof. Yong Tang and Prof. Zaozao Qiu in the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Dr. ZHAO Da, a PhD student worked in this project, was awarded the Springer Thesis Award.

Project Coordinator

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