29th Symposium on Chemistry Postgraduate Research in Hong Kong

Iridium-Catalyzed B(3,6)/B(4)-Alkenylation of *o*-Carborane *via* Vinylidene Rearrangement

Huifang Zhang[1,2], Zaozao Qiu*[,1] and Zuowei Xie*[1,3]

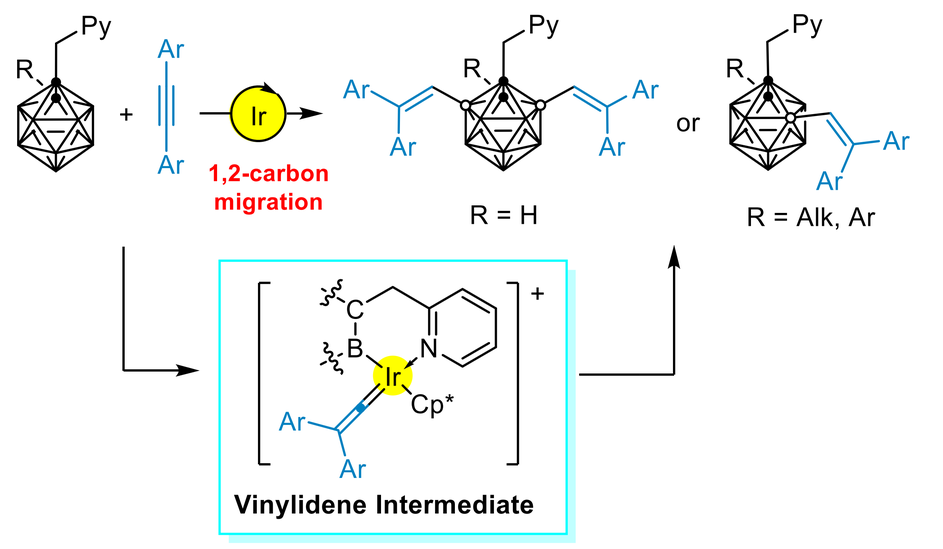
[1]*Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

[2]*Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China;*

[3]*Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, China*

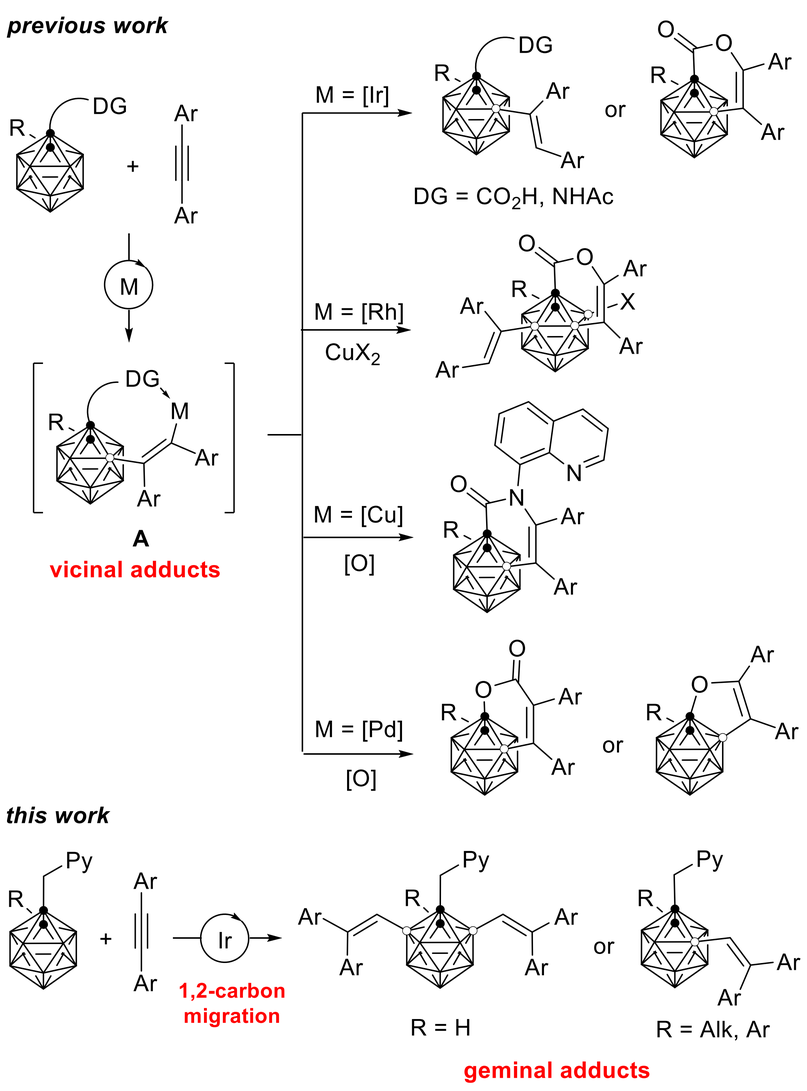
Introduction

Carboranes, a class of carbon–boron molecular clusters, are often viewed as three-dimensional analogues of benzene. They have been proved as very useful building blocks in supramolecular design, optoelectronics, nanomaterials, boron neutron capture therapy agents and organometallic/coordination chemistry due to their unusual thermal and chemical stabilities. Thus, functionalization of carboranes has received growing interest. However, the main challenge is to achieve selective activation among ten boron hydride vertices with very similar chemical environments.[1] We developed an efficient Ir-catalyzed cage boron vertex alkenylation of 1-(2'-picolyl)-*o*-carboranes with diarylacetylenes, leading to a wide variety of B–H geminal addition products via 1,2-carbon migration. The steric effect of cage carbon substituents has a great impact on the regioselectivity of such alkenylation reactions.

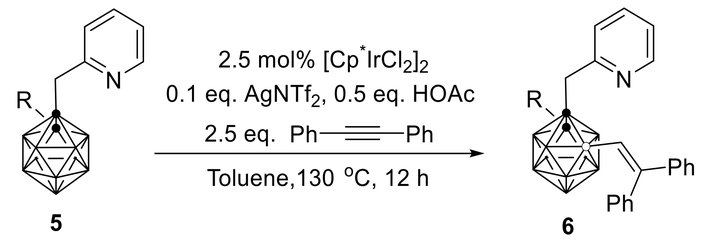


Transition metal catalyzed B–H activation of *o*-carboranes with diarylalkynes

For catalytic cage B–H alkenylation with diarylalkynes, different types of products are generated under various reaction conditions. Carboranes incorporated with a carboxy or acetylamino directing group at cage C(1) position lead to B(4)-alkenylation or B(4)/B(3)-alkenylation-annulation products under different conditions. It is suggested that the alkyne 1,2-insertion intermediate **A** is involved in these catalytic cycles to produce vicinal addition products. Herein, we report controlled synthesis of geminal adducts 3,6-$(Ar_2C{=}CH)_2$-*o*-carboranes (Ar = aryl) and 4-$(Ar_2C{=}CH)$-*o*-carboranes through an Ir-catalyzed cage B–H activation. This study represents a new catalytic functionalization of *o*-carboranes including vinylidene rearrangement of internal alkynes via 1,2-carbon migration.



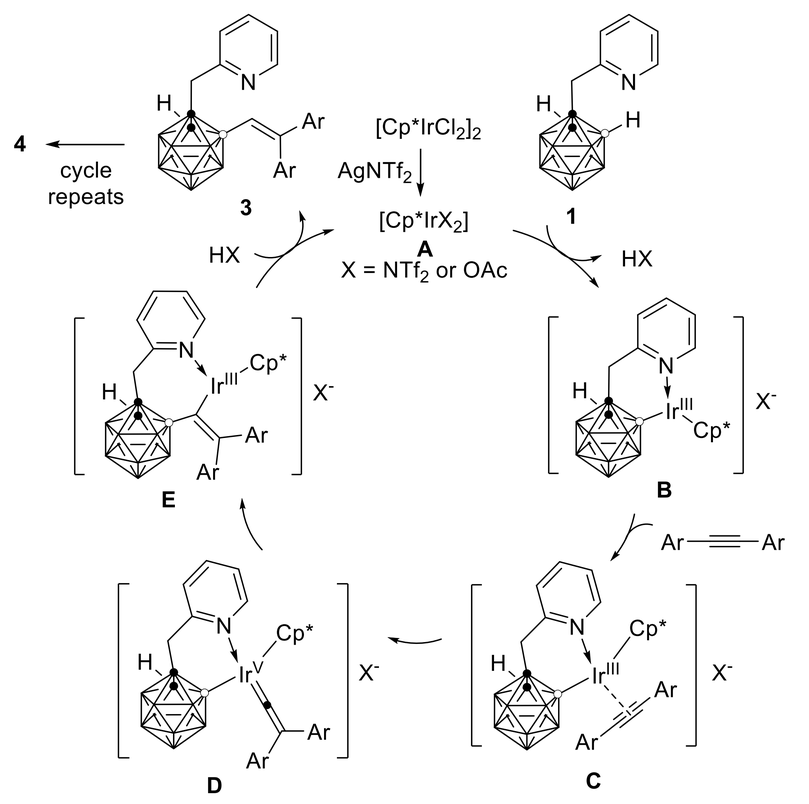
B(4)-alkenylation of 1-(2'-picolyl)-*o*-carboranes



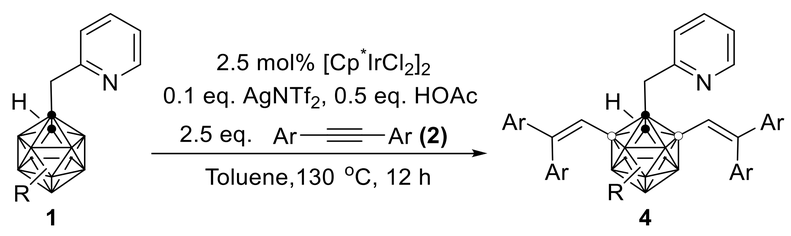
Entry[a]	R	Isolated Yield of **6** (%)
1	Me	99 (**6a**)
2	Et	98 (**6b**)
3	^{n}Bu	99 (**6c**)
4	Bn	98 (**6d**)
5	^{i}Pr	95 (**6e**)
6	Ph	95 (**6f**)

[a] All reactions were carried out on 0.2 mmol scale in 3 mL of toluene.

Proposed catalytic cycle



B(3,6)-dialkenylation of 1-(2'-picolyl)-*o*-carboranes



Entry[a]	R	Ar	Isolated Yield of **4** (%)
1	H	C_6H_5	90 (**4a**)
2	H	*p*-^{i}PrC$_6$H$_4$	91 (**4b**)
3	H	*p*-MeC$_6$H$_4$	95 (**4c**)
4	H	*p*-^{t}BuC$_6$H$_4$	92 (**4d**)
5	H	*p*-OMeC$_6$H$_4$	90 (**4e**)
6	H	*p*-FC$_6$H$_4$	75 (**4f**)
7	H	*p*-ClC$_6$H$_4$	62 (**4g**)
8	H	*m*-MeC$_6$H$_4$	84 (**4h**)
9[b]	H	*m*-^{i}PrC$_6$H$_4$	95 (**4i**)
10	H	*m*-OMeC$_6$H$_4$	91 (**4j**)
11	H	3,5-(OMe)$_2$C$_6$H$_3$	77 (**4k**)
12	H	*m*-PhC$_6$H$_4$	73 (**4l**)
13	H	*m*-FC$_6$H$_4$	62 (**4m**)
14	H	*m*-ClC$_6$H$_4$	58 (**4n**)
15	H	*o*-OMeC$_6$H$_4$	94 (**4o**)
16	H	*o*-FC$_6$H$_4$	60 (**4p**)
17[b]	H	2-Naphthyl	60 (**4q**)
18	9,12-(Me)$_2$	C_6H_5	98 (**4r**)

[a] All reactions were carried out on 0.2 mmol scale in 3 mL of toluene. [b] 1 eq. HOAc.

Reference

1. Qiu, Z.; Xie, Z. *Acc. Chem. Res.* **2021**, *54*, 4065-4079.

Acknowledgements

We acknowledge the financial supports from National Natural Sciences Foundation of China and Shanghai Science and Technology Committee.

Contact information

Huifang Zhang, zhanghuifang@sioc.ac.cn; Zaozao Qiu, qiuzz@sioc.ac.cn; Zuowei Xie, zxie@cuhk.edu.hk