

## Controlled synthesis of carbons-adjacent and -apart *nido*- and *arachno*-carborane anions and their metal complexes\*

Zuowei Xie

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

*Abstract:* The controlled synthesis of carborane anions is a difficult challenge and is of great interest to synthetic chemists. By varying the bridge length of cage carbons-linked *o*-carboranes, the two cage carbon atoms are locked in place during the reactions, leading to the controlled synthesis of *ortho*-, *meta*- and *para*-isomer of *nido*-carborane dianions. The isomers of *arachno*-carborane tetraanions can also be prepared in the controlled manner via changing the electronic configuration of the transition-metal ions or the bridge length. This article provides an overview of our recent work on this subject.

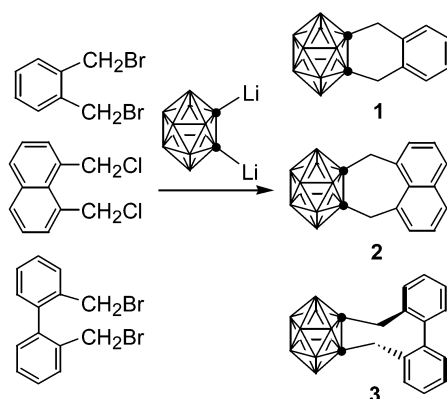
### INTRODUCTION

It is well documented that *o*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (R = H, alkyl, aryl) can be reduced by group 1 metals to give carbons-apart dianionic species [*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, which are very useful versatile synthons for the production of numerous metallocarboranes of s-, p-, d-, and f-elements [1]. This reduction process leads to the complete cleavage of the cage C–C bond. Excess alkali metals cannot directly drive *o*-carborane to *arachno*-carborane since the carbons-apart [*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> are much poorer electron acceptors than their neutral counterparts [1,2]. Electrochemical data indicate that the arrangement of the cage carbon atoms has large influences on the chemical properties of carborane cage compounds, and carbons-adjacent isomers are generally more reactive than their carbons-apart ones [3]. Thus, carbons-adjacent carborane anions may lead to metallocarborane complexes with higher reactivities and thus are amenable to further chemistry.

The controlled synthesis of carborane anions becomes a difficult challenge and is of great interest to synthetic chemists. To control the positions of two cage carbon atoms of an *o*-carborane during the reduction processes, the most effective and easiest way is probably to introduce a proper linkage between the two cage carbon atoms forcing them in place. With this in mind, we have prepared three cage carbons-linked *o*-carboranes with different bridge lengths, shown in Scheme 1. We report herein a detailed study on the reactivity patterns of these model compounds and controlled synthesis of different isomers of carborane dianions and tetraanions.

---

\*Lecture presented at the XI<sup>th</sup> International Meeting on Boron Chemistry (IMEBORON XI), Moscow, Russia, 28 July–2 August 2002. Other presentations are published in this issue, pp. 1157–1355.



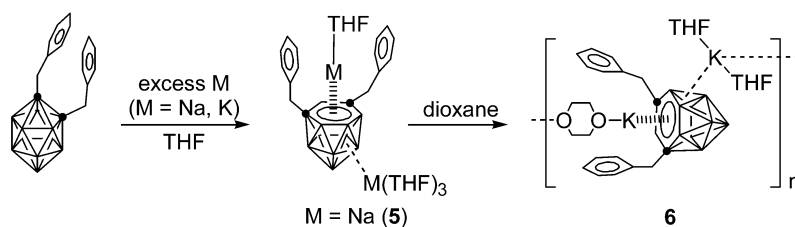
Scheme 1

### CAGE CARBONS-LINKED *o*-CARBORANES

The  $pK_a$  value of  $o$ - $C_2B_{10}H_{12}$  is  $\sim 23$  [4]. Thus, the cage C–H is readily deprotonated by  $n$ -BuLi to form the corresponding dilithium salt  $[C_2B_{10}H_{10}]Li_2$ , which makes the derivatization of  $o$ -carborane possible. Treatment of  $[C_2B_{10}H_{10}]Li_2$  with 1,2- $C_6H_4(CH_2Br)_2$ , 1,8- $C_{10}H_6(CH_2Cl)_2$ , or 1,1'-( $C_6H_4$ ) $_2$ -2,2'-( $CH_2Br$ ) $_2$  gives the corresponding cage carbons-linked  $o$ -carboranes  $\mu$ -1,2-[ $o$ - $C_6H_4(CH_2)_2$ ]-1,2- $C_2B_{10}H_{10}$  (**1**),  $\mu$ -1,2-[1,8- $C_{10}H_6(CH_2)_2$ ]-1,2- $C_2B_{10}H_{10}$  (**2**), or  $\mu$ -1,2-[1,1'-( $C_6H_4$ ) $_2$ -2,2'-( $CH_2$ ) $_2$ ]-1,2- $C_2B_{10}H_{10}$  (**3**), respectively (Scheme 1). These three model compounds bear a six-, seven-, or eight-membered inner ring constructed by the cage and the aromatic moiety, respectively, which enables us to investigate the relationships between the bridge length and the cage C–C bond cleavage during reductive processes [5].

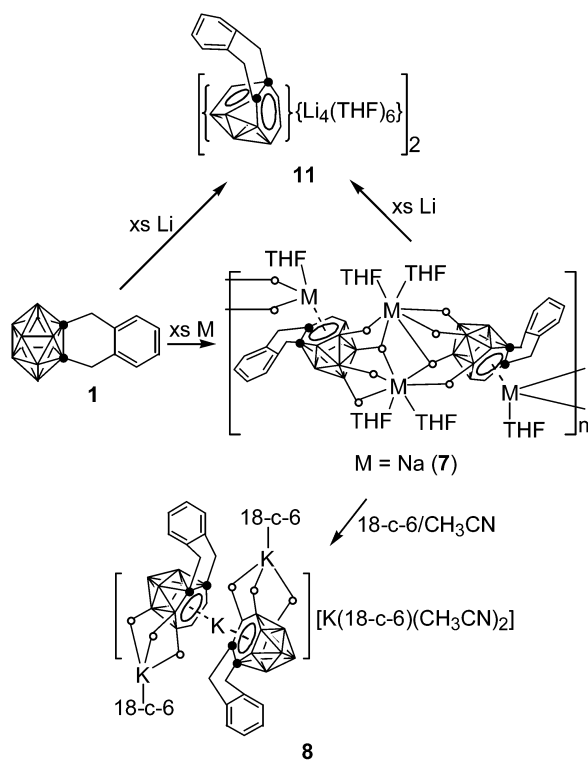
### CONTROLLED SYNTHESIS OF *NIDO*-CARBORANE DIANIONS

Reaction of 1,2-( $C_6H_5CH_2$ ) $_2$ -1,2- $C_2B_{10}H_{10}$  (**4**) with excess finely cut Na or K metal in THF gives the group 1 salts of *nido*-carborane dianion,  $[(C_6H_5CH_2)_2C_2B_{10}H_{10}]M_2(THF)_4$ , in which the two cage carbon atoms are in *meta* positions (called *m*-isomer), shown in Scheme 2 [6]. In general, only *m*-isomers of *nido*-carborane dianions are isolated from the reduction of the cage carbon-unlinked  $o$ -carboranes [1].

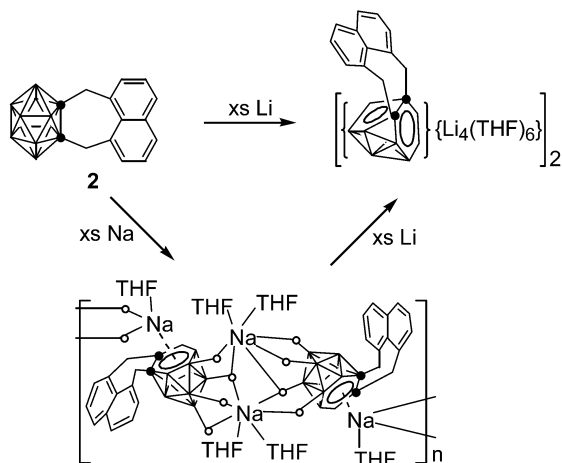


Scheme 2

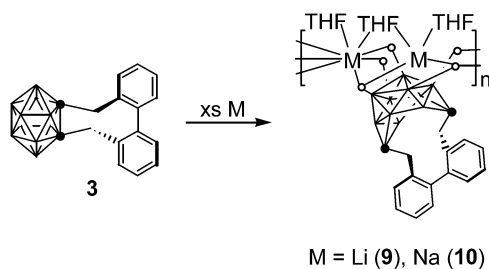
Treatment of **1** with excess finely cut Na or K metal in THF affords a half-sandwich complex  $[\{\mu$ -1,2-[ $o$ - $C_6H_4(CH_2)_2$ ]-1,2- $C_2B_{10}H_{10}\}_2Na_4(THF)_6]_n$  (**7**) or a full-sandwich complex  $[\{\mu$ -1,2-[ $o$ - $C_6H_4(CH_2)_2$ ]-1,2- $C_2B_{10}H_{10}\}_2K_3(18\text{-crown-6})_2][K(18\text{-crown-6})(CH_3CN)_2]$  (**8**) after recrystallization from proper solutions, respectively (Scheme 3). X-ray analyses indicate that the cage carbon atom adjacency is maintained during the reductive process; namely, an *ortho*-isomer (*o*-isomer) of *nido*-


**Scheme 3**

carborane dianion is generated [7,8]. Interaction of **2** with excess Na metal also produces the carbons-adjacent *nido*-carborane dianion (*o*-isomer), shown in Scheme 4.


**Scheme 4**

Compound **3** reacts with excess Na metal in THF to give a carbons-apart *nido*-carborane dianionic salt  $[\{\mu\text{-}1,4\text{-}[1,1'\text{-}(\text{C}_6\text{H}_4)_2\text{-}2,2'\text{-}(\text{CH}_2)_2\text{-}1,4\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{M}_2(\text{THF})_3\}]_n$  [ $\text{M} = \text{Li}$  (**9**),  $\text{Na}$  (**10**)] in which the two cage carbon atoms are in *para* positions (*p*-isomer) (Scheme 5). Its structure has been confirmed by single-crystal X-ray analyses [5].



Scheme 5

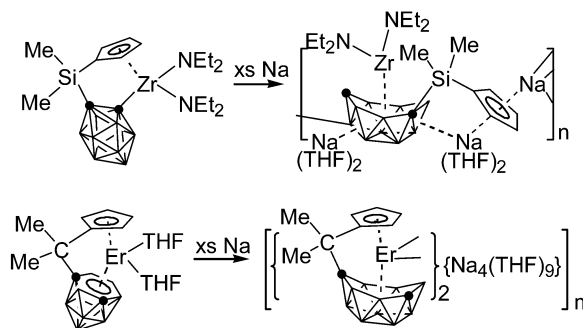
The above results show that (1) if the number of the bridging carbon atoms between two cage carbon atoms of an *o*-carborane is five or less, the cage carbon atom adjacency is maintained during the reductive process giving *o*-isomer; (2) if this number is six or more, the cage carbon–carbon bond is completely broken, giving “carbons-apart” carborane anion in which the two cage carbon atoms are in *para* positions (*p*-isomer); and (3) in the absence of the linkage, “carbons-apart” carborane anions in which the cage carbon atoms are in *meta* positions (*m*-isomer) are often isolated during the reductive processes. Thus, three isomers of *nido*-carborane dianion of the  $C_2B_{10}$  system (shown in Chart 1) can be synthesized in the controlled manner. The effects of the bridge length on the cage carbon–carbon bond cleavage are very obvious. Of course, the rigidity of the bridge may also affect the cage carbon–carbon bond cleavage.



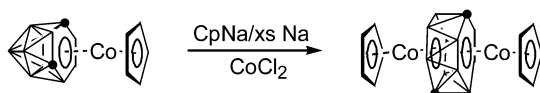
Chart 1

### CONTROLLED SYNTHESIS OF ARACHNO-CARBORANE TETRAANIONS

The carbons-apart *nido*-carborane moiety in the 13-vertex metallacarboranes of d- and f-elements is able to accept two more electrons from group 1 metals to form the *arachno*-carborane species because the highly electropositive transition-metal ions can enhance the electron-accepting ability of the cage. However, the molecular structures of the resultant *arachno*-carborane complexes are dependent upon the electronic configuration of the central metal ions. For  $d^0/f^n$  transition-metal ions, the *arachno*-carborane tetraanions with a basket shape are always generated regardless of the transition-metal ions, the cage substituents, solvents and reducing agents. Examples are given in Scheme 6 [9–12]. For  $d^n$  metal ions such as  $Co^{3+}$ , a bicapped hexagonal antiprism *arachno*-carborane tetraanion is resulted (Scheme 7) [13]. The reasons caused this isomerization of the *arachno*-carborane cage are probably due to the 18-electron rule [11]. The  $\eta^7-C_2B_{10}H_{12}^{4-}$  bears a seven-membered open face offering five pairs of elec-



Scheme 6



Scheme 7

trons to the bonding with metal ions, while  $(\eta^6:\eta^6)\text{-C}_2\text{B}_{10}\text{H}_{12}^{4-}$  possesses two six-membered bonding faces. It is noteworthy that these carbons-apart *arachno*-carborane isomers are stabilized by the transition-metal ions and cannot be isolated as simple ionic salts, which limits further exploration. We then extend our research to carbons-adjacent *arachno*-carborane chemistry.

Treatment of carbons-adjacent *nido*-carborane complex  $[\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{Na}_4(\text{THF})_6]_n$  (**7**) with excess Li metal offers carbons-adjacent *arachno*-carborane tetraanionic salt  $[\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_6]_2$  (**11**). It can also be prepared from the reaction of **1** with excess Li metal (Scheme 3). Single-crystal X-ray analyses reveal that it consists of one open six-membered  $\text{C}_2\text{B}_4$  face and one open five-membered  $\text{C}_2\text{B}_3$  face that share one common edge of the cage C–C bond [7]. These results show that the carbons-adjacent *arachno*-carborane has very different structural features from its carbons-apart isomers.

Reaction of **2** with excess Li metal also gives carbons-adjacent *arachno*-carborane tetraanionic salt  $[\{\mu\text{-}1,2\text{-}[1,8\text{-C}_{10}\text{H}_6(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_6]_2$ . Under the same reaction conditions, however, interaction of **3** with excess Li metal only produces carbons-apart *nido*-carborane dianionic salt  $[\{\mu\text{-}1,4\text{-}[1,1'\text{-}(\text{C}_6\text{H}_4)_2\text{-}2,2'\text{-}(\text{CH}_2)_2]\text{-}1,4\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_2(\text{THF})_3]_n$ . These results clearly suggest that the carbons-adjacent carboranes are more reactive than their carbons-apart isomers.

Thus, the controlled synthesis of three isomers of *arachno*-carborane tetraanion of the  $\text{C}_2\text{B}_{10}$  system (shown in Chart 2) can be achieved by varying the bridge length of the cage carbons-linked *o*-carboranes or changing the electronic configuration of the transition-metal ions.

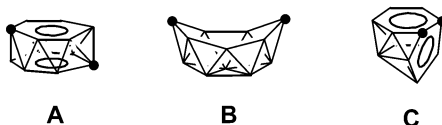
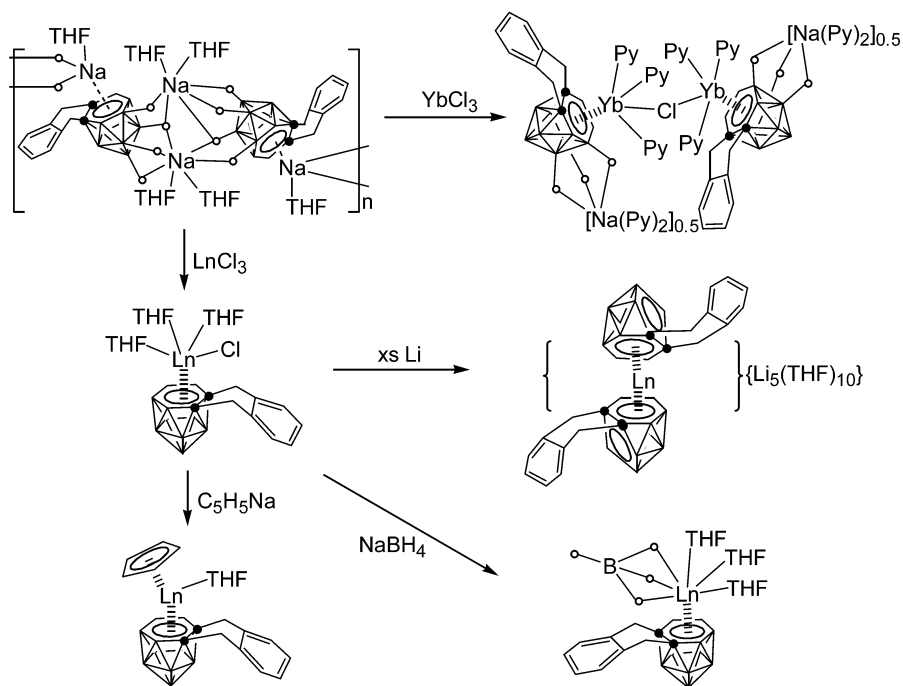


Chart 2

## CARBONS-ADJACENT METALLACARBORANES

The alkali metal salts of carbons-adjacent *nido*- and *arachno*-carborane anions are useful synthons for the production of a variety of carbons-adjacent metallacarboranes [14]. Interaction of  $[\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{Na}_4(\text{THF})_6]_n$  (**7**) with 2 equiv of  $\text{LnCl}_3$  gives novel half-sandwich lanthanacarboranes  $[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{LnCl}(\text{THF})_3$  (Ln = Nd (**12**), Er (**13**), Y (**14**)). Under the similar reaction conditions, treatment of  $\text{YbCl}_3$  with **7** in a molar ratio of 2:1 in THF, however, results in the formation of organoytterbium(II) complex  $[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Yb}(\text{NC}_5\text{H}_5)_3\{\text{Na}(\text{NC}_5\text{H}_5)_2\}_{0.5}\text{]}\mu\text{-Cl}$  (**15**), which suggests that **7** can reduce  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$ .

These half-sandwich lanthanacarboranes bear a reactive Ln–Cl bond, which makes them very important starting materials for the synthesis of complexes containing Ln–C, Ln–H and Ln–heteroatom bonds. For example, reaction of **12** with 1 equiv of  $\text{NaBH}_4$  or  $\text{C}_5\text{H}_5\text{Na}$  affords  $[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Nd}[(\mu\text{-H})_3\text{BH}](\text{THF})_3$  or  $[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Nd}(\eta^5\text{-C}_5\text{H}_5)(\text{THF})$ , respectively. Interaction of **13** with excess Li metal leads to the isolation of full-sandwich complexes  $[\eta^6\text{-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{Er}][\text{Li}_5(\text{THF})_{10}]$ . This can also be prepared from the reaction of *arachno*-species  $[\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2]\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_6]_2$  (**11**) with  $\text{ErCl}_3$  in THF. These transformations are outlined in Scheme 8.



Scheme 8

## CONCLUSIONS

The controlled synthesis of *o*-, *m*- and *p*-isomer of *nido*-carborane dianions can be achieved via variation in the bridge length between the two cage carbon atoms of *o*-carboranes. Various isomers of *arachno*-carborane tetraanions can also be prepared in the controlled manner by changing the electronic configuration of the central transition metal ions or the bridge length of the cage carbons-linked *o*-carboranes.

Carbons-adjacent *nido*-carborane dianions are more reactive than their carbons-apart counterparts and can be directly reduced by lithium metal to form the carbons-adjacent *arachno*-carborane tetraanions. They are useful versatile synthons for the production of a new class of carbons-adjacent metallocarboranes. The carbons-adjacent *arachno*-carborane tetraanions may also be useful building blocks for the generation of multi-sandwich metallocarboranes since they possess two adjacent six- and five-membered bonding faces.

## ACKNOWLEDGMENTS

I am greatly indebted to every one of my motivated and talented graduate students and postdoctoral associates. Their cheerful dedication and hard work are a never-ending source of pleasure for me. I thank the Research Grants Council of the Hong Kong Special Administration Region, Direct Grant and Chemistry Department of the Chinese University of Hong Kong for financial support.

## REFERENCES

- (a) R. N. Grimes. In *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson (Eds.), Vol. 1, Chap. 9, Pergamon, Oxford (1995); (b) A. K. Saxena and N. S. Hosmane. *Chem. Rev.* **93**, 1081 (1993); (c) Z. Xie. *Coord. Chem. Rev.* **231**, 23 (2002).

2. K. Hermansson, M. Wójcik, S. Sjöberg. *Inorg. Chem.* **38**, 6039 (1999).
3. J. H. Morris, H. J. Gysling, D. Reed. *Chem. Rev.* **85**, 51 (1985).
4. A. I. Shatenshtein, L. I. Zakharkin, E. S. Petrov, E. A. Yakoleva, F. S. Yakushin, Z. Vukmirovich, G. G. Isaeva, V. N. Kalinin. *J. Organomet. Chem.* **23**, 313 (1970).
5. G. Zi, H.-W. Li, Z. Xie. *Organometallics* **21**, 5415 (2002).
6. K. Chui, H.-W. Li, Z. Xie. *Organometallics* **19**, 5447 (2000).
7. G. Zi, H.-W. Li, Z. Xie. *Organometallics* **20**, 3836 (2001).
8. G. Zi, H.-W. Li, Z. Xie. *Chem. Commun.* 1110 (2001).
9. Z. Xie, C. Yan, Q. Yang, T. C. W. Mak. *Angew. Chem., Int. Ed.* **38**, 1761 (1999).
10. (a) Z. Xie, K. Chui, Q. Yang, T. C. W. Mak. *Organometallics* **18**, 3947 (1999). (b) K. Chui, Q. Yang, T. C. W. Mak, Z. Xie. *Organometallics* **19**, 1391 (2000).
11. K. Chui, Q. Yang, T. C. W. Mak, W. H. Lam, Z. Lin, Z. Xie. *J. Am. Chem. Soc.* **122**, 5758 (2000).
12. Y. Wang, H. Wang, H.-W. Li, Z. Xie. *Organometallics* **21**, 3311 (2002).
13. W. J. Evans, M. F. Hawthorne. *J. Chem. Soc., Chem. Commun.* 38 (1974).
14. G. Zi, H.-W. Li, Z. Xie. *Organometallics* **21**, 3464 (2002).