

Palladium/Nickel-Cocatalyzed Cycloaddition of 1,3-Dehydro-*o*-Carborane with Alkynes. Facile Synthesis of C,B-Substituted Carboranes

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Abstract: *o*-Carboryne (1,2-dehydro-*o*-carborane) has been reported as a very reactive intermediate and regarded as a three-dimensional relative of benzyne, whereas the 1,3-dehydro-*o*-carborane has remained elusive. In this article, we present the preparation of 1,3-dehydro-*o*-carborane from 3-iodo-1-lithio-*o*-carborane mediated by palladium(0). This reactive intermediate can be trapped by alkynes via Pd/Ni-cocatalyzed [2 + 2 + 2] cycloaddition reaction, leading to the formation of C,B-substituted-*o*-carborane derivatives. The possible reaction mechanism involving the formation of metal-1,3-dehydro-*o*-carborane followed by stepwise insertions of 2 equiv of alkyne and reductive elimination is proposed, and the relative reactivity of M–C versus M–B bond in metal-1,3-dehydro-*o*-carborane complexes is also discussed. This work offers a new methodology for B-functionalization of carboranes and demonstrates that metal-1,3-dehydro-*o*-carborane can be viewed as a new kind of boron nucleophile.

Introduction

o-Carboryne (1,2-dehydro-*o*-carborane), a three-dimensional relative of benzyne (Chart 1), was first reported as a very reactive intermediate in 1990.¹ It can react with alkenes, dienes, alkynes, and aromatics in [2 + 2], [4 + 2] cycloaddition and ene-reaction patterns,² similar to those of benzyne.³ This reactive species can be stabilized by transition metals, leading to the formation of metal-*o*-carboryne complexes.⁴ Molecular orbital calculations on the Zr-carboryne complex suggest that the bonding interactions between the Zr atom and carboryne ligand are best described as a resonance hybrid of both the Zr–C σ and Zr–C π bonding forms (Chart 2),^{4b} which is similar to that

Chart 1. Benzyne, *o*-Carboryne, and 1,3-Dehydro-*o*-carborane

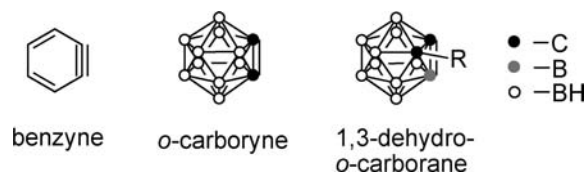
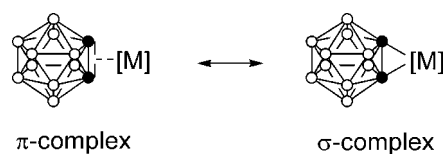


Chart 2. Bonding Description of Metal-Carboryne Complex



- (1) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4082–4083.
- (2) (a) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C. M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313–1318. (b) Huang, Q.; Gingrich, H. L.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254–3257. (c) Cunningham, R. J.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1994**, *33*, 4811–4812. (d) Ho, D. M.; Cunningham, R. J.; Brewer, J. A.; Bian, N.; Jones, M., Jr. *Inorg. Chem.* **1995**, *34*, 5274–5278. (e) Barnett-Thamattoor, L.; Zheng, G.; Ho, D. M.; Jones, M., Jr.; Jackson, J. E. *Inorg. Chem.* **1996**, *35*, 7311–7315. (f) Jeon, J.; Kitamura, T.; Yoo, B.-W.; Kang, S. O.; Ko, J. *Chem. Commun.* **2001**, 2110–2111. (g) Lee, T.; Jeon, J.; Song, K. H.; Jung, I.; Baik, C.; Park, K.-M.; Lee, S. S.; Kang, S. O.; Ko, J. *Dalton Trans.* **2004**, 933–937. (h) Wang, S. R.; Qiu, Z.; Xie, Z. *J. Am. Chem. Soc.* **2010**, *132*, 9988–9989.
- (3) (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Franzen, V.; Joschek, H. I. *Ann.* **1967**, *703*, 90–95. (c) Jones, M., Jr.; Levin, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 6411–6415.
- (4) (a) Saylor, A. A.; Beall, H.; Sieckhaus, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 5790–5792. (b) Wang, H.; Li, H.-W.; Huang, X.; Lin, Z.; Xie, Z. *Angew. Chem., Int. Ed.* **2003**, *42*, 4347–4349. (c) Ren, S.; Deng, L.; Chan, H.-S.; Xie, Z. *Organometallics* **2009**, *28*, 5749–5756. (d) Qiu, Z.; Deng, L.; Chan, H.-S.; Xie, Z. *Organometallics* **2010**, *29*, 4541–4547.

observed in Zr-benzyne complex.⁵ This type of metal-*o*-carboryne complex can react with unsaturated molecules in a controlled manner to produce alkenylcarboranes,⁶ benzocarboranes,⁷ dihydrobenzocarboranes,⁸ and other functionalized carboranes.⁹

Theoretical studies suggest that the formation of *o*-carboryne is energetically very comparable to that of benzyne. The

- (5) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411–7413.
- (6) Qiu, Z.; Xie, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 6572–6575.
- (7) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2006**, *128*, 7728–7729.
- (8) Qiu, Z.; Xie, Z. *J. Am. Chem. Soc.* **2009**, *131*, 2084–2085.
- (9) (a) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2005**, *127*, 13774–13775. (b) Ren, S.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2009**, *131*, 3862–3863. (c) Ren, S.; Chan, H.-S.; Xie, Z. *Organometallics* **2009**, *28*, 4106–4114.

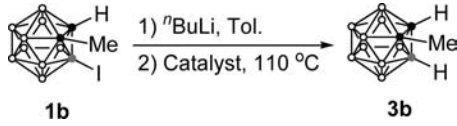
calculated cage C–C bond distance in *o*-carboryne is 1.356 Å, indicating the multiple bond character.¹⁰ We wondered if the unknown species 1,3-dehydro-*o*-carborane could be generated. It might feature a cage C–B multiple bond (Chart 1). In view of the characteristics of *o*-carboryne and the important application of boron-centered nucleophiles,¹¹ we then initiated a research program to explore the chemistry of 1,3-dehydro-*o*-carborane.

As *o*-carboryne can be generated in situ by heating 1-Li-2-X-1,2-C₂B₁₀H₁₀ (X = Br,^{1,2} I¹²) via the elimination of LiX, we attempted to produce 1,3-dehydro-*o*-carborane in a similar manner using 1-Li-3-X-1,2-C₂B₁₀H₁₀ as precursors. Unfortunately, both 1-Li-3-X-1,2-C₂B₁₀H₁₀ and 1-Li-2-CH₃-3-X-1,2-C₂B₁₀H₉ are all very thermally stable even after prolonged heating in THF or toluene. Considering that the cage B–I bond can undergo oxidative addition in the presence of Pd(0),¹³ we speculated that an oxidative addition of the cage B–I in 1-Li-3-I-1,2-C₂B₁₀H₁₀ on Pd(0), followed by a subsequent elimination of LiI, would afford the target complex Pd-1,3-dehydro-*o*-carborane, which could possibly be trapped by alkynes. Herein, we report our work on palladium/nickel-cocatalyzed reaction of 1,3-dehydro-*o*-carborane with 2 equiv of alkynes to afford [2 + 2 + 2] cycloaddition products, C,B-substituted carboranes.

Results and Discussion

1,3-Dehydro-*o*-Carborane. In an initial attempt, a toluene solution of 1-Li-2-Me-3-I-1,2-C₂B₁₀H₉, prepared in situ by treatment of 2-Me-3-I-1,2-C₂B₁₀H₁₀ (**1b**) with 1 equiv of ⁿBuLi, was heated in the presence of 10 mol % Pd(PPh₃)₄ to give 1-methyl-*o*-carborane (**3b**) in almost quantitative yield in 14 h as indicated by ¹¹B NMR spectrum of the reaction mixture. This catalytic deiodination may result from the thermal decomposition of Pd-2-methyl-1,3-dehydro-*o*-carborane presumably via radical process (Table 1, entry 1).^{2g,7} The solvent acts as the hydrogen source. If the catalyst loading was reduced to 5 mol %, the reaction was slowed down (Table 1, entry 2). Ni(cod)₂ (cod = 1,5-cyclooctadiene) was almost inactive in the activation of the cage B–I bond (Table 1, entry 4). However, a combination of 5 mol % of Ni(cod)₂ and 5 mol % of Pd(PPh₃)₄ can enhance the reaction rate (Table 1, entry 3) (vide infra). Grignard reagent (MeMgBr) is less effective than ⁿBuLi in the reaction with cage CH. On the other hand, MeMgBr is known to react with 3-iodo-*o*-carborane in the presence of Pd(0) to give 3-methyl-*o*-carborane.^{13a} It is noted that no reaction proceeded at *T* < 70 °C, and compound **3b** can only be generated at higher tem-

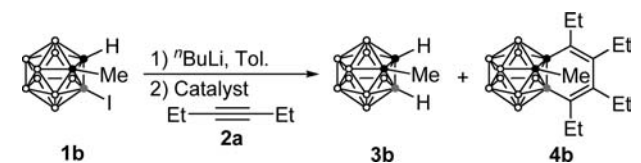
Table 1. Catalytic Deiodination of 1-Li-2-Me-3-I-1,2-C₂B₁₀H₉^a



entry	catalyst	loading (mol %)	reaction time (h)	yield (%) ^b	
				1b	3b
1	Pd(PPh ₃) ₄	10	14	<1	>99
2	Pd(PPh ₃) ₄	5	30	10	90
3	Pd(PPh ₃) ₄ /Ni(cod) ₂	5/5	30	<1	>99
4	Ni(cod) ₂	5	30	>99	<1

^a Conditions: (1) ⁿBuLi (1 equiv), toluene, r.t., 0.5 h; (2) catalyst, 110 °C. ^b Yields determined by GC-MS on the crude product mixture.

Table 2. Optimization of Pd/Ni-Cocatalyzed Cycloaddition Reaction^a



entry	catalyst	loading (mol %)	reaction time	yield ^b		
				1b	3b	4b
1	none	0	7 d	100		
2	Pd(OAc) ₂	10	3 d	56	19	25
3	PdCl ₂ (PPh ₃) ₂	10	3 d	9	12	79
4	PdCl ₂ (cod)	10	3 d	87	12	<1
5	PdCl ₂ (cod)/2PPh ₃	10	30 h	<1	8	91
6	Pd(CH ₂ TMS) ₂ (cod)	10	3 d	90	9	<1
7	[Pd(Ally)Cl] ₂	5	3 d	6	25	69
8	[Pd(Ally)Cl] ₂ /4PPh ₃	5	1 h	<1	7	92
9	Pd(dba) ₂	10	7 d	21	36	43
10	Pd(PPh ₃) ₄	10	7 h	2	8	90
11	Ni(cod) ₂	10	7 d	72	13	15
12	Pd(PPh ₃) ₄ /Ni(PPh ₃) ₄	10/10	3 h	3	6	91
13	Pd(dba) ₂ /Ni(cod) ₂	10/10	3 d	25	43	32
14	Pd(PPh ₃) ₄ /Ni(cod) ₂	10/10	0.5 h	<1	6	93
15	Pd(PPh ₃) ₄ /Ni(cod) ₂	5/5	2 h	<1	3	96
16	Pd(PPh ₃) ₄ /Ni(cod) ₂ /2PPh ₃	5/5	2 h	<1	4	95
17	Pd(PPh ₃) ₄ /Ni(cod) ₂	2/2	4 h	<1	6	93
18	PdCl ₂ (PPh ₃) ₂ /Ni(cod) ₂	10/10	3 h	9	7	84

^a Conditions: (1) ⁿBuLi (1 equiv), toluene, r.t., 0.5 h; (2) catalyst, 3-hexyne (4 equiv), 110 °C. ^b Yields determined by GC-MS on the crude product mixture.

peratures as indicated by ¹¹B NMR spectroscopy in the reaction of 1-Li-2-Me-3-I-1,2-C₂B₁₀H₉ with a catalytic amount of Pd-(PPh₃)₄. Many attempts to isolate pure (η²-1,3-*o*-C₂B₁₀H₉Me)Pd(L), an analogue of (η²-1,2-*o*-C₂B₁₀H₁₀)Ni(L),^{4a} from a stoichiometric reaction in the presence of PPh₃ or dppe (dppe = 1,2-bis(diphenylphosphino)ethane) failed as the reaction did not occur at *T* < 70 °C and the resultant metal complex slowly decomposed at higher temperatures. It is noteworthy that 3-bromo-*o*-carborane and 3-chloro-*o*-carborane are incompatible with this reaction because the oxidative addition between the B–Br or B–Cl bond and Pd(0) is inefficient.¹⁴

Subsequent work focused on trapping the 1,3-dehydro-*o*-carborane intermediate by 3-hexyne. The optimization of this reaction was listed in Table 2. No reaction was observed after heating at 110 °C for 7 days in the absence of a catalyst. Most of the Pd(II) species examined can catalyze the [2 + 2 + 2]

(14) Viñas, C.; Barberà, G.; Oliva, J. M.; Teixidor, F.; Welch, A. J.; Rosair, G. M. *Inorg. Chem.* **2001**, *40*, 6555–6562.

- (10) Kiran, B.; Anoop, A.; Jemmis, E. D. *J. Am. Chem. Soc.* **2002**, *124*, 4402–4407.
- (11) (a) Braunschweig, H.; Dewhurst, R. D.; Schneider, A. *Chem. Rev.* **2010**, *110*, 3924–3957. (b) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890–931. (c) Hartwig, J. F. *Nature* **2008**, *455*, 314–322. (d) Coombs, D. L.; Aldridge, S. *Coord. Chem. Rev.* **2004**, *248*, 535–559. (e) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1–51. (f) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685–2722. (g) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786–1801. (h) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113–115. (i) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079. (j) Spokoiny, A. M.; Reuter, M. G.; Stern, C. L.; Ratner, M. A.; Seideman, T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2009**, *131*, 9482–9483.
- (12) Qiu, Z.; Wang, S. R.; Xie, Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 4649–4652.
- (13) (a) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866–4868. (b) Eriksson, L.; Winberg, K. J.; Claro, R. T.; Sjöberg, S. J. *Org. Chem.* **2003**, *68*, 3569–3573.

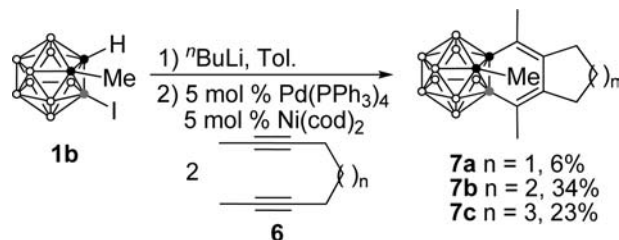
Table 3. Pd/Ni-Cocatalyzed Cycloaddition of 1,3-Dehydro-*o*-carborane with Alkynes^a

entry	R ¹ /1	R ² /R ³ /2	product	yield (%) ^b
1	H/ 1a	Et/Et/ 2a	4a	12
2	Me/ 1b	Et/Et/ 2a	4b	79
3	ⁿ Bu/ 1c	Et/Et/ 2a	4c	67
4	TMS/ 1d	Et/Et/ 2a	4d	69
5	Ph/ 1e	Et/Et/ 2a	4e	43
6	(CH ₂) ₂ OMe/ 1f	Et/Et/ 2a	4f	58
7	(CH ₂) ₂ NMe ₂ / 1g	Et/Et/ 2a	4g	51
8	Me/ 1b	ⁿ Pr/ ⁿ Pr/ 2b	4h	55
9	Me/ 1b	ⁿ Bu/ ⁿ Bu/ 2c	4i	43
10	Me/ 1b	ⁿ Bu/TMS/ 2d	3b	85
11	Me/ 1b	COOMe/COOMe/ 2e	NR ^c	
12	Me/ 1b	Me/COOMe/ 2f	NR ^c	
13	Me/ 1b	Ph/Ph/ 2g	4j	55
14	Me/ 1b	<i>p</i> -tolyl/ <i>p</i> -tolyl/ 2h	4k	51
15	Me/ 1b	<i>o</i> -tolyl/ <i>o</i> -tolyl/ 2i	3b	83
16	Me/ 1b	Me/Ph/ 2j	4l+5l	49 (4l/5l = 62/38) ^d
17	Me/ 1b	Et/Ph/ 2k	4m+5m	47 (4m/5m = 80/20) ^d

^a Conditions: (1) ⁿBuLi (1 equiv), toluene, r.t., 0.5 h; (2) Pd(PPh₃)₄ (5 mol %), Ni(cod)₂ (5 mol %), alkyne (4 equiv), 110 °C, overnight. ^b Isolated yields. ^c **1** was recovered. ^d Ratio was determined by ¹H NMR spectroscopy on the crude product mixture.

cycloaddition reaction of 2-methyl-1,3-dehydro-*o*-carborane with 2 equiv of 3-hexyne to afford 1,3-benzocarborane **4b** (entries 2–8). Addition of PPh₃ to PdCl₂(cod) or [Pd(Ally)Cl]₂ led to a significant improvement of the reactions probably due to the effective reduction of Pd(II) to Pd(0) by PPh₃ (entries 5 and 8).¹⁵ In fact, Pd(PPh₃)₄ can catalyze the [2 + 2 + 2] cycloaddition reaction, affording **4b** in 90% yield (entry 10). Pd(dba)₂ (dba = dibenzylideneacetone), however, gave **4b** in 43% yield even after prolonged heating, suggesting large ligand effects (entry 9). On the other hand, Ni(cod)₂ exhibited very low catalytic activity (entry 11), but the addition of nickel(0) species to palladium catalyst can significantly accelerate the reactions (entries 12–18).¹⁶ The combination of Pd(PPh₃)₄ with Ni(cod)₂ exhibited the highest catalytic activity. If the catalyst loading was decreased from 10 mol % to 2 mol %, the reaction rate was slowed down, but the yield still remained very high (entries 14–17). Ni(cod)₂ can also accelerate the catalytic reaction of PdCl₂(PPh₃)₂, giving **4b** in 84% yield in 3 h (entry 18).

Various alkynes were compatible with this palladium/nickel-cocatalyzed cycloaddition reaction under the optimal conditions (Table 2, entry 15). The results were compiled in Table 3. 1,3-Dehydro-*o*-carborane without a substituent at 2-C position gave a very low isolated yield (12%) of **4a**, whereas 2-methyl-1,3-dehydro-*o*-carborane afforded **4b** in 79% isolated yield (entry 1 vs 2). Steric effects of substituents on the 2-C position of the cage were much less significant than electronic effects; for example, the electron-withdrawing group phenyl led to a big drop in the yield of **4e** (entries 5 vs 2–4). Both aliphatic and aromatic alkynes underwent [2 + 2 + 2] cycloaddition reactions, and steric factors of alkynes played an important role in such reactions. No cycloaddition reaction proceeded for sterically

Scheme 1. Pd/Ni-Cocatalyzed Cycloaddition of 1,3-Dehydro-*o*-carborane with Diynes

more demanding alkynes bearing a trimethylsilyl or *o*-tolyl group, in which only the deiodination product **3b** was observed (entries 10 and 15). Alkynes bearing a carbonyl group such as **2e** and **2f** were incompatible with this reaction because they reacted with the carboryne precursor 1-Li-2-Me-3-I-1,2-C₂B₁₀H₉ (entries 11 and 12). Unsymmetrical alkynes **2j,k** gave two isomers of **4l,m** and **5l,m** with **4** being the major ones (entries 16 and 17).

The palladium/nickel-cocatalyzed cycloaddition reaction was also extended to diynes (Scheme 1). Under the same reaction condition mentioned above, 2-methyl-1,3-dehydro-*o*-carborane underwent cycloaddition with diynes **6** to provide the 1,3-benzo-*o*-carboranes, **7a–c** in 6–34% yields with a good fused-ring size tolerance. A dimerization product of **6a** was isolated from the reaction mixture, which probably resulted in the rather low yield for the five-membered ring system **7a**.

All products were fully characterized by ¹H, ¹³C, and ¹¹B NMR spectra, high-resolution mass spectrometry as well as elemental analyses. In the ¹H NMR spectrum of **4a**, the cage CH signal was overlapped with that of CH₂ of the Et groups at 2.63 ppm when CDCl₃ was used as solvent, whereas a clear broad singlet corresponding to the cage CH was observed at 1.83 ppm in benzene-*d*₆. The cage C–CH₃ and cage C–Si(CH₃)₃ protons appeared as singlet each at 1.29 and 0.03 ppm, respectively, in the ¹H NMR spectra of **4b** and **4d**. The ¹³C NMR spectra of **4**, **5**, and **7** showed two peaks in the range 70–80 ppm assignable to the two cage carbons and three olefinic carbon resonances in the period 120–150 ppm, respectively. The olefinic carbon bonded to the cage boron atom was not observed probably due to the quadrupolar broadening effect.¹⁷ The ¹¹B{¹H} NMR spectra exhibited a 3:5:2 pattern spanning between –7 to –13 ppm for **4b,h–m**, **5**, and **7**, whereas 1:2:1:3:1:1:1, 3:4:1:1:1, 1:4:3:1:1, 2:1:1:3:3, 1:1:5:1:1:1, and 3:5:1:1 patterns were observed for those of **4a,c,d,e,f,g**, respectively. It is noteworthy that the signal of the BC vertex was overlapped with the BH signals and was unable to be identified in the ¹H coupled ¹¹B NMR spectra.

The molecular structures of **4a,b,d,j,m**, **5m**, and **7b** were further confirmed by single-crystal X-ray analyses (Figure 1). Table 4 summarizes the selected bond distances. The six-membered C₅B ring is coplanar in these molecules with alternative short and long bonds, similar to those observed in 1,2-benzocarboranes.^{7,12} These data suggest that there is no substantial π -delocalization in such rings. Thus, the C₄ unit may be best described as a butadiene moiety.

Reaction Mechanism. As shown in Table 1, a catalytic amount of Pd(0) species can quantitatively convert 1-Li-2-Me-3-I-1,2-C₂B₁₀H₉ to **3b** in refluxing toluene. On the other hand, refluxing **1b** and 4 equiv of 3-hexyne in toluene in the

(15) Miyaura, M. Cross-Coupling Reactions. A Practical Guide. In *Topics in Current Chemistry*; Springer: Berlin Heidelberg, 2002.

(16) Cho, C. S.; Lee, J. W.; Lee, D. Y.; Shim, S. C.; Kim, T. J. *Chem. Commun.* **1996**, 2115–2116.

(17) Cook, K. S.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 5411–5418.

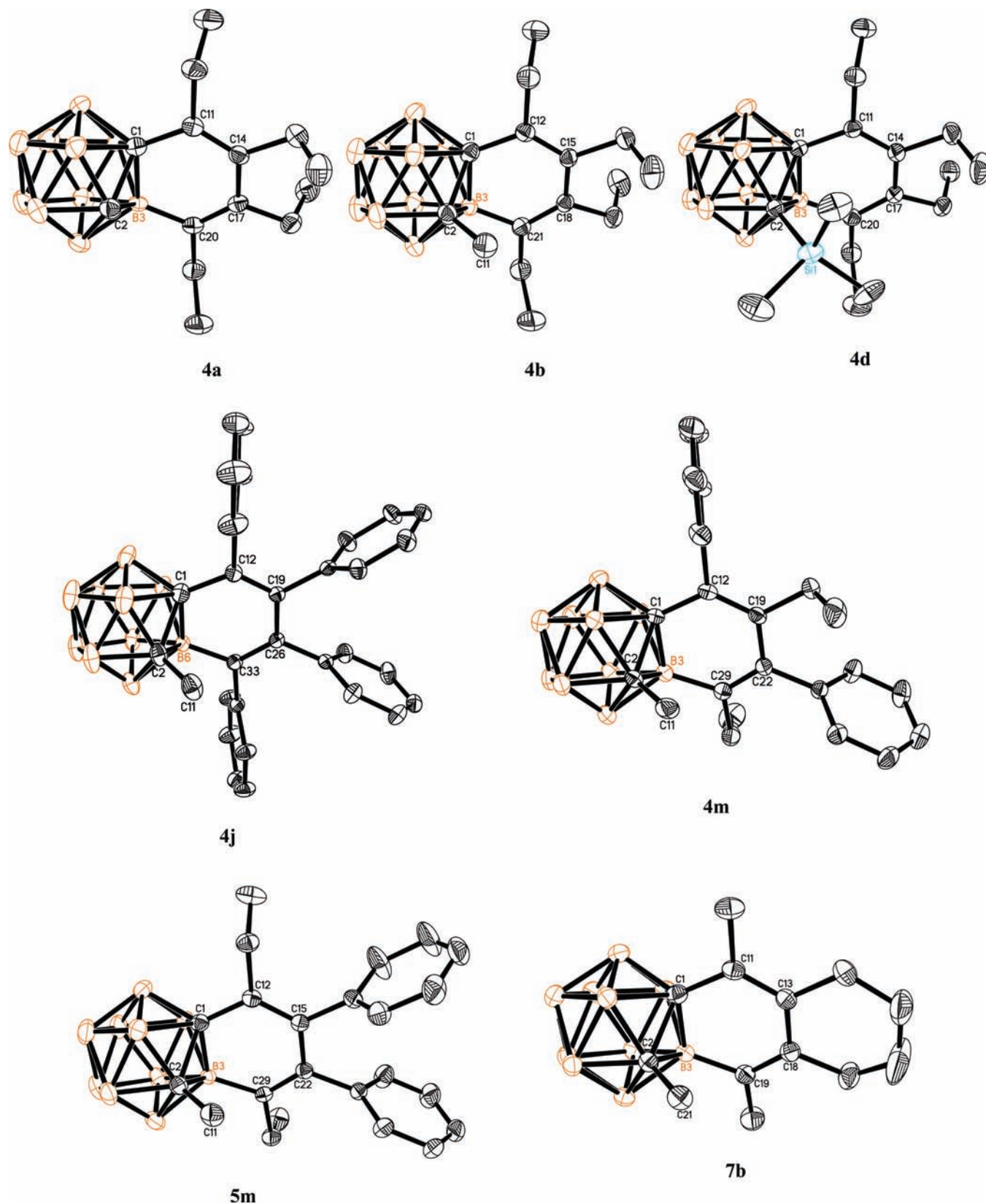
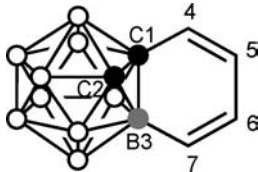


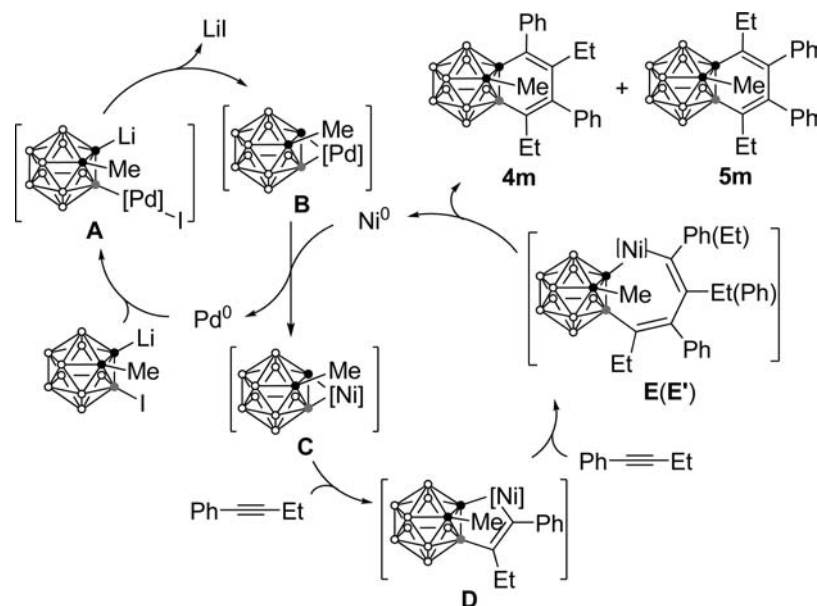
Figure 1. Molecular Structures of **4a**, **4b**, **4d**, **4j**, **5m**, and **7b**.

presence of 5 mol % $\text{Pd}(\text{PPh}_3)_4$ and 5 mol % $\text{Ni}(\text{cod})_2$ or 1 equiv of $\text{Pd}(\text{PPh}_3)_4$ and $\text{Ni}(\text{cod})_2$ did not give any alkyne insertion products; rather, it afforded the isomers of **1b** with iodo being located at different cage boron positions as indicated by GC-MS analyses. These results suggest that the

cage B–I can undergo oxidative addition reaction on $\text{Pd}(0)$ and the resultant cage B–Pd(I) bond is inert toward 3-hexyne. Thus, it is most likely that the above [2 + 2 + 2] cycloaddition reactions proceed through a metal-1,3-dehydro-*o*-carborane intermediate.

Table 4. Selected Bond Lengths (Å) in **4a**, **4b**, **4d**, **4j**, **5m** and **7b**


	4a	4b	4d	4j	4m	5m	7b
C(1)–C(2)	1.680(4)	1.728(4)	1.726(2)	1.723(4)	1.684(5)	1.721(4)	1.722(5)
C(1)–B(3)	1.706(5)	1.708(4)	1.707(2)	1.706(4)	1.707(5)	1.701(4)	1.689(5)
C(1)–C(4)	1.507(4)	1.502(4)	1.518(2)	1.520(4)	1.481(5)	1.514(4)	1.508(5)
C(4)–C(5)	1.340(4)	1.353(4)	1.366(3)	1.347(3)	1.350(4)	1.352(4)	1.359(5)
C(5)–C(6)	1.482(4)	1.479(4)	1.498(2)	1.487(3)	1.481(5)	1.492(4)	1.483(5)
C(6)–C(7)	1.351(4)	1.351(4)	1.366(3)	1.357(3)	1.344(5)	1.351(4)	1.356(5)
C(7)–B(3)	1.524(5)	1.527(5)	1.546(3)	1.527(4)	1.537(6)	1.531(4)	1.533(5)

Scheme 2. Proposed Mechanism for Pd/Ni-Cocatalyzed [2 + 2 + 2] Cycloaddition Reaction

Having the aforementioned experimental data, a plausible mechanism for palladium/nickel-cocatalyzed [2 + 2 + 2] cycloaddition is proposed in Scheme 2. Since Ni(0) can hardly insert into the B–I bond (Table 1, entry 4), the Pd-1,3-dehydro-*o*-carborane **B** is formed by the oxidative addition of B–I on Pd(0), followed by LiI elimination. As a two-component catalyst system is much more effective than Pd species alone in the reaction of 1,3-dehydro-*o*-carborane with alkynes, it is rational to propose a transmetalation process between Pd and Ni,¹⁸ affording a more reactive nickel-1,3-dehydro-*o*-carborane **C**. This hypothesis was supported by the following experiments. An 1:1 mixture of (η^2 -*o*-C₂B₁₀H₁₀)Pd(PPh₃)₂^{4d,19} and Ni(cod)₂ in toluene at room temperature afforded (η^2 -*o*-C₂B₁₀H₁₀)-Ni(PPh₃)₂^{4a} as indicated by ³¹P NMR. On the other hand, (η^2 -*o*-C₂B₁₀H₁₀)Pd(PPh₃)₂ did not show any activity toward 3-hexyne. However, the addition of 20 mol % of Ni(cod)₂ to the above solution led to the isolation of [2 + 2 + 2] cycloaddition product 1,2-{1',4'-[EtC=C(Et)-C(Et)=C(Et)]}-1,2-C₂B₁₀H₁₀⁷ in 18%

yield. The relatively higher activity of the Ni species may probably be ascribed to the fact that the Pd–B bond is stronger than the Ni–B bond or the Ni–B bonding pair is more nucleophilic than that of Pd–B.²⁰ In the reaction with PhC≡CEt, the electronically controlled regioselective insertion of unsymmetrical alkyne²¹ into the Ni–B bond gives the nickelacyclopentene intermediate **D**. The absence of 2-Me-1,3-{1',4'-[EtC=C(C₆H₅)-C(Et)=C(C₆H₅)]}-1,2-C₂B₁₀H₁₀ in the products indicates the exclusive insertion into the Ni–B bond. This is consistent with the results reported in the literature.^{17,20,22} As an M–B bond is much more nucleophilic than an M–C bond,²⁰ the alkyne insertion into an M–B bond could be considered as a nucleophilic attack of the M–B σ -bond (the bonding electron pair) on one of the two alkyne carbons. The nucleophilic attack in nature also explains the regioselectivity observed in the unsymmetrical alkynes; that is, in the insertion product **D**, boron is bonded to the carbon having electron-donating ethyl substituent. Since the insertion of alkynes into the M–C(cage) bond

(18) Reduction potentials: Ni²⁺/Ni = –0.25 V, Pd²⁺/Pd = 0.95 V, see Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*; Pearson Education: New York, 2001, pp 752–754.

(19) Deng, L. Synthesis, structural characterization and reactivity study of novel twelve-, thirteen-, and fourteen-vertex carboranes and their derivatives. Ph.D. Thesis. The Chinese University of Hong Kong, 2006.

(20) Dang, L.; Lin, Z.; Marder, T. B. *Chem. Commun.* **2009**, 3987–3995.

(21) (a) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, *14*, 1267–1277. (b) Bennett, M. A.; Macgregor, S. A.; Wenger, E. *Helv. Chim. Acta* **2001**, *84*, 3084–3104.

(22) Selander, N.; Willy, B.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4051–4053.

in metal-carboranyl complexes is prohibited due to steric reasons,²³ the second equivalent of alkyne inserts into the Ni–C(vinyl) bond in both a head-to-tail (major) and head-to-head (minor) manner. Subsequent reductive elimination yields the final products **4m/5m** (80/20) and regenerates the Ni(0) to complete the catalytic cycle. Compound **4m** is the major isomer although the regioselectivity in the second insertion is relatively poor.

Conclusion

We have shown for the first time the generation of 1,3-dehydro-*o*-carborane, which can be regarded as a new kind of boron nucleophile. This reactive species can be trapped by alkynes in the presence of a catalytic amount of transition metals. The present work offers a new methodology for C,B-functionalization of carboranes and demonstrates the relative reactivity of cage M–C versus M–B bond in metal-1,3-dehydro-*o*-carborane complexes toward alkynes.

Experimental Section

General Procedures. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. ¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz. ¹³C{¹H} NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 spectrometer at 100 MHz. ¹¹B{¹H} NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 96 MHz or a Bruker DPX 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Melting points were determined using an Electro-thermal M-IA9000 melting point apparatus and the values reported were uncorrected. NiCl₂(PPh₃)₂,²⁴ 3-iodo-*o*-carborane (**1a**),^{13a} 3-iodo-1-methyl-*o*-carborane (**1b**),¹⁴ and 3-iodo-1-phenyl-*o*-carborane (**1e**)¹⁴ were prepared according to the literature procedures. Alkynes were freshly distilled from CaH₂ or P₂O₅ prior to use. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

3-Iodo-1-*n*-butyl-*o*-carborane (1c). To an ether solution (5 mL) of 3-iodo-*o*-carborane (**1a**; 400 mg, 1.5 mmol) was added ⁿBuLi (1.6 M, 0.93 mL, 1.5 mmol) and the mixture was stirred at 0 °C for 1 h. After adding ⁿBuBr (0.16 mL, 1.5 mmol), the reaction mixture was stirred for 5 h at 0 °C and then hydrolyzed with water. The organic layer was separated, dried over MgSO₄, and concentrated. The residue was subject to column chromatography on silica gel (230–400 mesh) using hexane as eluent to give **1c** as a colorless oil (254 mg, 53%). ¹H NMR (400 MHz, CDCl₃): δ 3.61 (s, 1H) (cage H), 2.47 (m, 1H), 2.30 (m, 1H), 1.50 (m, 2H), 1.35 (m, 2H) (CH₂), 0.94 (t, *J* = 7.2 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 75.0, 64.7 (cage C), 38.9, 30.9, 22.0 (CH₂), 13.6 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.6 (1B), -5.2 (1B), -7.5 (1B), -10.0 (1B), -11.3 (4B), -13.3 (1B), -25.3 (1B). HRMS: *m/z* calcd for C₆H₁₉B₁₀I⁺: 326.1529. Found: 326.1532. Anal. Calcd for C₆H₁₉B₁₀I: C, 22.09; H, 5.87. Found: C, 22.42; H, 5.76.

3-Iodo-1-trimethylsilyl-*o*-carborane (1d). This compound was prepared as a white solid from Me₃SiCl using the same procedures as reported for **1c**. Yield: 87%. Mp: 74.2–74.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.64 (s, 1H) (cage H), 0.41 (s, 9H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 67.4, 64.1 (cage C), -0.9 (CH₃). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -0.2 (1B), -1.7 (1B), -4.7 (1B), -9.0 (2B), -9.7 (1B), -11.0 (1B), -12.1 (1B), -13.0 (1B), -28.1 (1B). HRMS: *m/z* calcd for C₅H₂₀B₁₀ISi⁺ ([M + H]⁺): 342.1298. Found: 342.1302. Anal. Calcd for C₅H₁₉B₁₀ISi: C, 17.54; H, 5.59. Found: C, 17.41; H, 5.49.

3-Iodo-1-methoxyethyl-*o*-carborane (1f). This compound was prepared as colorless oil from 2-chloroethyl methyl ether using the same procedures reported for **1c**. Yield: 85%. ¹H NMR (400 MHz, CDCl₃): δ 3.87 (s, 1H) (cage H), 3.56 (m, 2H) (OCH₂), 3.32 (s, 3H) (OCH₃), 2.79 (m, 1H), 2.63 (m, 1H) (OCH₂CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 72.8, 64.4 (cage C), 70.0 (OCH₂), 58.7 (OCH₃), 38.3 (OCH₂CH₂). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.2 (1B), -4.7 (1B), -7.7 (1B), -9.7 (1B), -11.3 (4B), -12.9 (1B), -24.5 (1B). HRMS: *m/z* calcd for C₅H₁₇B₁₀IO⁺: 328.1322. Found: 328.1323. Anal. Calcd for C₅H₁₇B₁₀IO: C, 18.30; H, 5.22. Found: C, 18.68; H, 5.14.

3-Iodo-1-dimethylaminoethyl-*o*-carborane (1g). This compound was prepared as light yellow oil from 2-chloro-*N,N*-dimethylethylamine using the same procedures reported for **1c**. Yield: 66%. ¹H NMR (400 MHz, CDCl₃): δ 4.00 (s, 1H) (cage H), 2.59 (m, 2H), 2.41 (m, 2H) (CH₂), 2.23 (s, 6H) (N(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 73.7, 64.4 (cage C), 57.8 (NCH₂), 45.4 (NCH₃), 35.8 (CH₂CH₂N). ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -1.9 (1B), -4.3 (1B), -7.4 (1B), -9.5 (1B), -11.0 (4B), -12.5 (1B), -24.2 (1B). HRMS: *m/z* calcd for C₆H₂₀B₁₀IN⁺: 341.1638. Found: 341.1639. Anal. Calcd for C₆H₂₀B₁₀IN: C, 21.12; H, 5.91; N, 4.10. Found: C, 21.59; H, 6.03; N, 3.83.

Palladium/Nickel-Cocatalyzed Cycloaddition Reaction of 1,3-Dehydro-*o*-carborane with Alkynes. A Representative Procedure. To a toluene solution (5 mL) of 2-Me-3-I-1,2-C₂B₁₀H₁₀ (0.5 mmol) was added 1 equiv of ⁿBuLi (0.5 mmol), and the reaction mixture was stirred at room temperature for 0.5 h. After addition of Pd(PPh₃)₄ (5 mol %), Ni(cod)₂ (5 mol %), and alkyne (2.0 mmol) [or diyne (1.0 mmol)], the reaction vessel was closed and heated at 110 °C overnight. The reaction was quenched with water and extracted with ether. After removal of organic solvents, the residue was subject to column chromatography on silica gel (230–400 mesh) using hexane as eluent to give the cycloaddition product, 1,3-benzo-*o*-carborane.

1,3-(1,2,3,4-Tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4a). Yield: 12%. Colorless crystals. Mp: 88.9–90.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.61 (m, 4H), 2.39 (m, 5H) (cage CH & CH₂), 1.19 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H), (CH₃). ¹H NMR (400 MHz, benzene-*d*₆): δ 2.54 (q, *J* = 7.6 Hz, 2H), 2.23 (m, 2H), 2.15 (m, 2H), 2.02 (m, 2H) (CH₂), 1.83 (s, 1H) (cage CH), 1.15 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.6 Hz, 3H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.74 (t, *J* = 7.6 Hz, 3H), (CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 143.3, 142.0, 130.6 (olefinic C), 60.4 (cage C), 28.3, 27.0, 23.3, 21.9 (CH₂), 15.5, 15.1, 15.0, 14.8 (CH₃), the olefinic C connected to the cage B atom and another cage C were not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -4.8 (1B), -7.8 (2B), -10.0 (1B), -11.7 (3B), -13.2 (1B), -14.0 (1B), -16.8 (1B). HRMS: *m/z* calcd for C₁₄H₃₀B₁₀⁺: 306.3345. Found: 306.3349. Anal. Calcd for C₁₄H₃₀B₁₀: C, 54.86; H, 9.87. Found: C, 54.80; H, 10.17.

2-Methyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4b). Yield: 54%. Colorless crystals. Mp: 129.2–130.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.54 (m, 3H), 2.44 (m, 5H) (CH₂), 1.29 (s, 3H) (CH₃), 1.15 (t, *J* = 7.6 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H) (CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.6, 143.5, 128.8 (olefinic C), 81.3, 67.9 (cage C), 28.2, 26.9, 23.5, 21.9 (CH₂), 20.2 (CH₃).

(23) (a) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259–272. (b) Sun, Y.; Chan, H.-S.; Zhao, H.; Lin, Z.; Xie, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 5533–5536. (c) Sun, Y.; Chan, H.-S.; Xie, Z. *Organometallics* **2006**, *25*, 3447–3453. (d) Qiu, Z.; Xie, Z. *Sci. China Ser. B-Chem.* **2009**, *52*, 1544–1558. (e) Shen, H.; Xie, Z. *Chem. Commun.* **2009**, 2431–2445.

(24) Venanzi, L. M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 137–142.

15.6, 15.3, 15.2, 14.7 (CH₂CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -8.0 (3B), -9.9 (1B), -11.2 (3B), -12.8 (1B), -14.4 (2B). HRMS: *m/z* calcd for C₁₅H₃₂B₁₀⁺: 320.3502. Found: 320.3504. Anal. Calcd for C₁₅H₃₂B₁₀: C, 56.21; H, 10.06. Found: C, 56.16; H, 10.15.

2-*n*-Butyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4c). Yield: 67%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 2.43 (m, 10H), 1.33 (m, 2H), 1.25 (m, 2H) (CH₂), 1.15 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.8, 143.3, 128.7 (olefinic C), 82.9, 72.7 (cage C), 31.4, 31.2, 28.1, 27.0, 23.5, 22.4, 21.8 (CH₂), 15.4, 15.3, 15.2, 14.8, 13.6 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -7.8 (3B), -11.2 (5B), -14.4 (1B), -16.2 (1B). HRMS: *m/z* calcd for C₁₈H₃₈B₁₀⁺: 362.3971. Found: 362.3967. Anal. Calcd for C₁₈H₃₈B₁₀: C, 59.62; H, 10.56. Found: C, 59.82; H, 10.72.

2-Trimethylsilyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4d). Yield: 69%. Colorless crystals. Mp: 109.0–110.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.46 (m, 8H) (CH₂), 1.26 (t, *J* = 7.6 Hz, 3H), 1.18 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.06 (t, *J* = 7.6 Hz, 3H) (CH₂CH₃), 0.03 (s, 9H) (Si(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.4, 142.2, 131.5 (olefinic C), 83.8, 68.5 (cage C), 29.0, 27.8, 23.5, 21.8 (CH₂), 15.2, 15.0, 14.7, 14.6 (CH₂CH₃), 0.56 (Si(CH₃)₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.6 (1B), -7.2 (2B), -7.8 (2B), -11.1 (3B), -12.3 (1B), -14.3 (1B). HRMS: *m/z* calcd for C₁₇H₃₈B₁₀Si⁺: 378.3740. Found: 378.3748. Anal. Calcd for C₁₇H₃₈B₁₀Si: C, 53.92; H, 10.11. Found: C, 53.91; H, 10.16.

2-Phenyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4e). Yield: 43%. Colorless crystals. Mp: 100.2–101.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.24 (m, 3H), 7.14 (m, 2H) (Ph), 2.63 (m, 4H), 2.13 (m, 3H), 1.98 (m, 1H) (CH₂), 1.27 (t, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.64 (t, *J* = 7.6 Hz, 3H), 0.49 (t, *J* = 7.6 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.3, 143.4, 130.3, 129.9, 129.4, 128.8, 127.4 (olefinic C & Ph), 84.9, 75.5 (cage C), 28.5, 27.5, 23.1, 21.6 (CH₂), 15.0, 14.7, 14.6, 14.0 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -6.0 (2B), -7.6 (1B), -10.0 (1B), -11.4 (3B), -13.7 (3B). HRMS: *m/z* calcd for C₂₀H₃₄B₁₀⁺: 382.3658. Found: 382.3657. Anal. Calcd for C₂₀H₃₄B₁₀: C, 62.79; H, 8.96. Found: C, 62.80; H, 8.96.

2-Methoxyethyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4f). Yield: 58%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 3.25 (t, *J* = 7.2 Hz, 2H) (OCH₂), 3.23 (s, 3H) (OCH₃), 2.52 (m, 3H), 2.38 (m, 5H), 1.64 (m, 2H) (CH₂), 1.16 (t, *J* = 7.6 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.0, 143.6, 128.7 (olefinic C), 82.8, 69.5 (cage C), 70.7 (OCH₂), 58.5 (OCH₃), 31.1, 28.2, 27.0, 23.5, 21.9 (CH₂), 15.4, 15.2, 15.1, 14.7 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -7.1 (1B), -7.8 (1B), -11.1 (5B), -12.7 (1B), -14.2 (1B), -16.1 (1B). HRMS: *m/z* calcd for C₁₇H₃₆B₁₀O⁺: 364.3764. Found: 364.3760. Anal. Calcd for C₁₇H₃₆B₁₀O: C, 56.01; H, 9.95. Found: C, 56.01; H, 9.96.

2-Dimethylaminoethyl-1,3-(1,2,3,4-tetraethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4g). Yield: 51%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 2.44 (m, 10H) (CH₂), 2.10 (s, 6H) (N(CH₃)₂), 1.54 (m, 2H) (CH₂), 1.16 (t, *J* = 7.6 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.0, 143.6, 128.7 (olefinic C), 83.1, 70.5 (cage C), 58.4 (NCH₂), 45.3 (N(CH₃)₂), 29.1, 28.2, 27.0, 23.5, 21.9 (CH₂), 15.5, 15.4, 15.3, 14.9 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -7.6 (3B), -10.9 (5B), -14.1 (1B), -16.2 (1B). HRMS: *m/z* calcd for C₁₈H₃₉B₁₀N⁺: 377.4080. Found:

377.4076. Anal. Calcd for C₁₈H₃₉B₁₀N: C, 57.25; H, 10.41; N, 3.71. Found: C, 57.32; H, 10.63; N, 3.53.

2-Methyl-1,3-(1,2,3,4-tetra-*n*-propyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4h). Yield: 55%. A white solid. Mp: 85.1–86.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.48 (m, 3H), 2.27 (m, 5H) (=CCH₂), 1.51 (m, 4H), 1.36 (m, 4H) (CH₂CH₂), 1.26 (s, 3H) (CH₃), 0.98 (m, 12H) (CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.4, 142.4, 127.8 (olefinic C), 81.3, 68.0 (cage C), 37.9, 36.5, 33.2, 31.6 (=CCH₂), 24.6, 24.2, 23.6 (CH₂CH₂), 20.2 (CH₃), 14.8, 14.7, 14.6, 14.4 (CH₂CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -8.3 (3B), -11.4 (5B), -14.6 (2B). HRMS: *m/z* calcd for C₁₉H₄₁B₁₀⁺ ([M+H]⁺): 376.4128. Found: 376.4114. Anal. Calcd for C₁₉H₄₀B₁₀: C, 60.59; H, 10.70. Found: C, 60.56; H, 10.84.

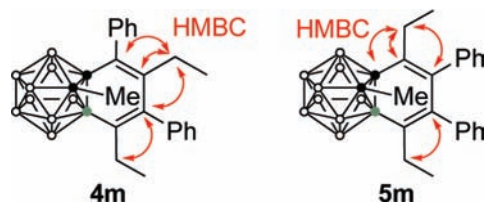
2-Methyl-1,3-(1,2,3,4-tetra-*n*-butyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4i). Yield: 33%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 2.48 (m, 3H), 2.31 (m, 5H), 1.40 (m, 16H) (CH₂), 1.27 (s, 3H) (CH₃), 0.95 (m, 12H) (CH₂CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 144.4, 142.3, 127.6 (olefinic C), 81.4, 68.0 (cage C), 35.4, 34.0, 33.4, 33.2, 32.9, 32.4, 30.7, 29.1, 23.4, 23.3, 23.2, 23.1 (CH₂), 20.2 (CH₃), 14.0, 13.9, 13.8, 13.7 (CH₂CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -8.4 (4B), -11.5 (4B), -14.6 (2B). HRMS: *m/z* calcd for C₂₃H₄₈B₁₀⁺: 432.4754. Found: 432.4758. Anal. Calcd for C₂₃H₄₈B₁₀: C, 63.84; H, 11.18. Found: C, 64.15; H, 11.62.

2-Methyl-1,3-(1,2,3,4-tetraphenyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4j). Yield: 55%. Yellow crystals. Mp: 251.7–252.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.09 (m, 9H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.77 (m, 10H) (aromatic CH), 2.12 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.5, 145.4, 142.2, 139.7, 139.5, 139.0, 131.9, 131.5, 130.4, 130.1, 129.7, 128.7, 127.5, 127.3, 127.2, 127.1, 126.8, 126.6, 126.5, 126.0, 125.9, 125.7 (aromatic and olefinic C), 78.7, 67.8 (cage C), 21.0 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -8.2 (3B), -10.5 (4B), -13.6 (3B). HRMS: *m/z* calcd for C₃₁H₃₂B₁₀⁺: 512.3502. Found: 512.3520. Anal. Calcd for C₃₁H₃₂B₁₀: C, 72.62; H, 6.29. Found: C, 72.68; H, 6.23.

2-Methyl-1,3-(1,2,3,4-tetra-*p*-tolyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4k). Yield: 51%. A white solid. Mp: 227.1–227.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.90 (m, 6H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.50 (m, 8H) (aromatic CH), 2.23 (s, 3H), 2.21 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.7, 145.5, 139.6, 137.0, 136.8, 136.5, 136.4, 135.1, 135.0, 134.8, 131.6, 131.3, 130.2, 129.9, 129.5, 128.6, 128.2, 127.9, 127.7, 127.5, 127.2 (aromatic and olefinic C), 79.1, 67.9 (cage C), 21.0, 20.9 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -7.8 (4B), -10.1 (4B), -13.3 (2B). HRMS: *m/z* calcd for C₃₅H₄₀B₁₀⁺: 568.4128. Found: 568.4150. Anal. Calcd for C₃₅H₄₀B₁₀: C, 73.91; H, 7.09. Found: C, 74.14; H, 7.38.

2-Methyl-1,3-(1,3-diphenyl-2,4-dimethyl-1,3-butadiene-1,4-diyl)-*o*-carborane (4l) + 2-Methyl-1,3-(1,4-dimethyl-2,3-diphenyl-1,3-butadiene-1,4-diyl)-*o*-carborane (5l). Yield: 49%. A white solid. **4l**: **5l** = 62: 38 by ¹H NMR spectrum of the crude mixture. Compound **4l** was isolated as a pure product whereas **5l** was always contaminated with **4l**. For **4l**: ¹H NMR (400 MHz, CDCl₃): δ 7.36 (m, 6H), 7.12 (m, 2H), 6.93 (m, 2H) (aromatic CH), 1.93 (s, 3H), 1.70 (s, 3H), 1.34 (s, 3H) (CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 144.8, 140.8, 139.8, 130.8, 129.6, 128.7, 128.5, 128.2, 128.1, 127.7, 126.9 (aromatic and olefinic C), 79.8, 67.9 (cage C), 22.9, 21.7, 20.5 (CH₃), the olefinic C connected to the cage B atom was not observed. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -7.3 (3B), -10.4 (5B), -13.2 (2B). HRMS: *m/z* calcd for C₂₁H₂₈B₁₀⁺: 388.3189. Found: 388.3189. Anal. Calcd for C₂₁H₂₈B₁₀: C, 64.92; H, 7.26. Found: C, 64.75; H, 7.33.

Scheme 3. The Correlations in HMBC Analyses of 4m and 5m



2-Methyl-1,3-(1,3-diphenyl-2,4-diethyl-1,3-butadiene-1,4-diyl)-o-carborane (4m) + 2-Methyl-1,3-(1,4-diethyl-2,3-diphenyl-1,3-butadiene-1,4-diyl)-o-carborane (5m). Yield: 47%. A white solid. **4m/5m** = 80:20 by ^1H NMR spectrum of the crude mixture. Both **4m** and **5m** were isolated in the pure form via many times of column chromatographic separation on silica gel. For **4m**: Mp: 128.5–130.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.32 (m, 6H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.16 (m, 1H), 7.06 (m, 1H), 6.97 (m, 1H) (aromatic CH), 2.27 (m, 2H), 1.78 (m, 2H) (CH_2), 1.73 (s, 3H) (CH_3), 1.01 (t, $J = 7.6$ Hz, 3H), 0.55 (t, $J = 7.6$ Hz, 3H) (CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 146.9, 144.7, 139.6, 139.2, 131.1, 129.9, 129.4, 128.0, 127.9, 127.8, 127.7, 127.6, 127.0 (aromatic and olefinic C), 79.7, 67.5 (cage C), 28.4, 26.8 (CH_2), 20.6 (CH_3), 14.3 (CH_2CH_3), the olefinic C connected to the cage B atom was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CDCl_3): δ -7.7 (3B), -10.9 (4B), -13.6 (3B). HRMS: m/z calcd for $\text{C}_{23}\text{H}_{32}\text{B}_{10}^+$: 416.3502. Found: 416.3489. Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{B}_{10}$: C, 66.31; H, 7.74. Found: C, 66.46; H, 7.91. For **5m**: Mp: 129.1–130.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.03 (m, 6H), 6.86 (d, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 6.4$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.61 (m, 1H) (aromatic CH), 2.23 (m, 4H) (CH_2), 1.71 (s, 3H) (CH_3), 0.98 (t, $J = 7.6$ Hz, 3H), 0.81 (t, $J = 7.6$ Hz, 3H) (CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 146.1, 144.8, 140.0, 130.6, 129.7, 129.6, 129.5, 129.1, 127.4, 127.3, 127.2, 126.4, 126.0 (aromatic and olefinic C), 80.7, 68.0 (cage C), 29.0, 28.2 (CH_2), 20.5 (CH_3), 14.5, 14.4 (CH_2CH_3), the olefinic C connected to the cage B atom was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CDCl_3): δ -7.4 (3B), -10.6 (4B), -13.6 (3B). HRMS: m/z calcd for $\text{C}_{23}\text{H}_{32}\text{B}_{10}^+$: 416.3502. Found: 416.3506. Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{B}_{10}$: C, 66.31; H, 7.74. Found: C, 66.52; H, 7.80. The regiochemical assignments of **4m** and **5m** were further confirmed by HMBC analyses and the diagnostic correlations are shown in Scheme 3.

2-Methyl-1,3-[1,4-dimethyl-2,3-(1,3-propanediyl)-1,3-butadiene-1,4-diyl]-o-carborane (7a). Yield: 6%. A white solid. Mp: 62.3–63.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.57 (m, 4H) ($=\text{CCH}_2$), 2.09

(s, 3H), 2.02 (s, 3H) ($=\text{CCH}_3$), 1.83 (m, 2H) (CH_2CH_2), 1.24 (s, 3H) (CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 147.2, 145.3, 118.7 (olefinic C), 81.7, 67.7 (cage C), 33.1, 31.3 ($=\text{CCH}_2$), 23.8 (CH_2CH_2), 20.3, 20.1, 19.5 (CH_3), the olefinic C connected to the cage B atom was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CDCl_3): δ -6.2 (1B), -7.3 (2B), -9.6 (1B), -11.0 (3B), -12.6 (1B), -13.8 (2B). HRMS: m/z calcd for $\text{C}_{12}\text{H}_{24}\text{B}_{10}^+$: 276.2876. Found: 276.2867. Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{B}_{10}$: C, 52.14; H, 8.75. Found: C, 52.39; H, 8.64.

2-Methyl-1,3-[1,4-dimethyl-2,3-(1,4-butanediyl)-1,3-butadiene-1,4-diyl]-o-carborane (7b). Yield: 34%. Colorless crystals. Mp: 127.5–128.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.45 (m, 4H) ($=\text{CCH}_2$), 2.11 (s, 3H), 2.04 (s, 3H) ($=\text{CCH}_3$), 1.65 (m, 4H) (CH_2CH_2), 1.23 (s, 3H) (CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 140.8, 139.0, 121.3 (olefinic C), 81.1, 67.4 (cage C), 29.3, 27.2 ($=\text{CCH}_2$), 22.1, 21.9 (CH_2CH_2), 21.0, 20.1, 19.3 (CH_3), the olefinic C connected to the cage B atom was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CDCl_3): δ -7.5 (3B), -9.3 (1B), -10.9 (3B), -12.2 (1B), -14.0 (2B). HRMS: m/z calcd for $\text{C}_{13}\text{H}_{26}\text{B}_{10}^+$: 290.3032. Found: 290.3029. Anal. Calcd for $\text{C}_{13}\text{H}_{26}\text{B}_{10}$: C, 53.76; H, 9.02. Found: C, 53.85; H, 9.28.

2-Methyl-1,3-[1,4-dimethyl-2,3-(1,5-pentenediyl)-1,3-butadiene-1,4-diyl]-o-carborane (7c). Yield: 23%. A white solid. Mp: 88.7–89.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 2.61 (m, 4H) ($=\text{CCH}_2$), 2.16 (s, 3H), 2.11 (s, 3H) ($=\text{CCH}_3$), 1.67 (m, 1H), 1.58 (m, 4H), 1.48 (m, 1H) (CH_2CH_2), 1.30 (s, 3H) (CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 146.0, 144.0, 124.4 (olefinic C), 81.1, 68.3 (cage C), 31.0, 29.0 ($=\text{CCH}_2$), 28.3, 28.0 (CH_2CH_2), 21.6, 20.2, 19.9 (CH_3), the olefinic C connected to the cage B atom was not observed. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CDCl_3): δ -7.9 (3B), -9.9 (1B), -11.2 (3B), -12.6 (1B), -14.4 (2B). HRMS: m/z calcd for $\text{C}_{14}\text{H}_{29}\text{B}_{10}^+$ ($[\text{M} + \text{H}]^+$): 304.3189. Found: 304.3179. Anal. Calcd for $\text{C}_{14}\text{H}_{29}\text{B}_{10}$: C, 55.23; H, 9.27. Found: C, 55.00; H, 9.58.

X-ray Structure Determination. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K α radiation. An empirical absorption correction was applied using the SADABS program.²⁵ All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.²⁶ The cage carbon atoms were located by comparing the bond lengths as the average distance between the carbon and carbon/boron atoms would appear shorter than that between the boron atoms. Crystal

Table 5. Crystal Data and Summary of Data Collection and Refinement

	4a	4b	4d	4j	4m	5m	7b
formula	$\text{C}_{14}\text{H}_{30}\text{B}_{10}$	$\text{C}_{15}\text{H}_{32}\text{B}_{10}$	$\text{C}_{17}\text{H}_{38}\text{B}_{10}\text{Si}$	$\text{C}_{31}\text{H}_{32}\text{B}_{10}$	$\text{C}_{23}\text{H}_{32}\text{B}_{10}$	$\text{C}_{23}\text{H}_{32}\text{B}_{10}$	$\text{C}_{13}\text{H}_{22}\text{B}_{10}$
crystal size (mm)	$0.50 \times 0.40 \times 0.30$	$0.40 \times 0.30 \times 0.20$	$0.50 \times 0.40 \times 0.30$	$0.50 \times 0.40 \times 0.30$	$0.40 \times 0.30 \times 0.20$	$0.50 \times 0.40 \times 0.30$	$0.50 \times 0.40 \times 0.30$
fw	306.48	320.51	378.66	512.67	416.59	416.59	286.41
crystal system	monoclinic	orthorhombic	orthorhombic	trigonal	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Pna_21	$P2_12_12_1$	$R\bar{3}$	$P2_1$	$P2_1/n$	$P2_1/c$
a , Å	9.626(6)	17.164(15)	9.771(3)	38.990(1)	12.641(1)	8.939(1)	9.311(6)
b , Å	17.645(12)	9.756(9)	14.550(5)	38.990(1)	8.951(1)	17.671(2)	7.728(5)
c , Å	12.048(8)	12.097(11)	16.814(6)	12.161(1)	22.288(2)	16.068(2)	24.422(16)
α , deg	90	90	90	90	90	90	90
β , deg	111.74(1)	90	90	90	98.53(1)	91.45(1)	91.05(1)
γ , deg	90	90	90	120	90	90	90
V , Å ³	1901(2)	2026(3)	2390(1)	16011(1)	2493.8(4)	2537.3(5)	1757(2)
Z	4	4	4	18	4	4	4
D_{calcd} , Mg/m ³	1.071	1.051	1.052	0.957	1.110	1.091	1.083
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2 θ range, deg	4.3 to 50.0	4.7 to 50.0	3.7 to 50.5	3.5 to 50.0	1.8 to 50.0	3.4 to 50.5	3.3 to 50.0
μ , mm ⁻¹	0.052	0.051	0.100	0.050	0.056	0.055	0.052
$F(000)$	656	688	816	4824	880	880	600
no. of obsd reflns	3355	2873	4328	6196	8299	4575	3092
no. of params refind	217	226	253	371	595	298	208
goodness of fit	1.044	1.082	1.049	1.056	1.001	1.094	1.035
R_1	0.075	0.048	0.039	0.069	0.052	0.082	0.090
wR_2	0.161	0.106	0.108	0.205	0.103	0.248	0.251

data and details of data collection and structure refinements are given in Table 5.

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- (25) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, 1996.
- (26) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: Madison, Wisconsin, USA, 1997.

tion Region (Project No. 404108) and The Chinese University of Hong Kong. We thank Ms. Hoi-Shan Chan for single-crystal X-ray analyses.

Supporting Information Available: Crystallographic data in CIF format for **4a**, **b**, **d**, **j**, **m**, **5m**, and **7b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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