ORGANOMETALLICS

Reaction of Carboryne with Alkylbenzenes

Sunewang Rixin Wang and Zuowei Xie*

Department of Chemistry and State Key Laboratory on Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Supporting Information

ABSTRACT: Carboryne (1,2-dehydro-*o*-carborane), in situ generated from the precursor 1-iodo-2-lithiocarborane, reacted with alkylbenzenes to give two regioisomers of the [4 + 2] cycloadducts as the major products in moderate to good yields, in which the steric factors play an important role in the regioselectivity. Minor products derived from benzylic C–H insertion reaction, annulation reaction, tandem [4 + 2] cycloaddition/homo Diels–Alder reaction, and tandem ene reaction/[2 + 2] cycloaddition were also isolated and characterized in the reaction of carboryne with toluene. The presence of AgF in the above reaction produced no notable changes in the product distributions and yields.



INTRODUCTION

Benzyne, a two-dimensional relative of carboryne (1,2-dehydroo-carborane), undergoes Diels–Alder reaction, ene reaction, and C–H bond insertion reaction with toluene and related derivatives.¹ Further addition of benzyne to the products of Diels–Alder reaction and the ene reaction occurs simultaneously under the reaction conditions, affording 2:1 or even 3:1 adducts (Scheme 1).¹ The ene reaction product is so reactive





that it cannot survive in the presence of excess benzyne, and only *o*-benzylbiphenyl, which results from the successive ene reactions of two benzyne molecules with one toluene, could be isolated. It is also documented that the coordination of silver cation onto the benzyne species significantly changes the reaction pathways of the above reactions, leading to the formation of biphenyls and benzocyclooctenes (Scheme 2).²

Carboryne $(o-C_2B_{10}H_{10}, 2)$, a very reactive intermediate reported first in 1990,³ is known to undergo [4 + 2]cycloaddition reaction with polycyclic and hetero aromatics,⁴ resembling that of benzyne.⁵ This reactive species can be generated from either 1-Br-2-Li-1,2-C₂B₁₀H₁₀³ or 1-Me₃Si-2-

Scheme 2. Reaction of Benzyne with Toluene in the Presence of Silver(I) Salt



[IPh(OAc)]-1,2- $C_2B_{10}H_{10}$.⁶ Recently, we reported a more efficient precursor, 1-I-2-Li-1,2- $C_2B_{10}H_{10}$ (1), for the production of 2.⁷ Our recent studies show that carboryne undergoes both [4 + 2] and [2 + 2] cycloaddition reactions with anisole and its derivatives. The resulting [2 + 2] cycloaddition intermediates can be converted to cyclooctatetraenocarboranes via thermal [3,3] sigmatropic rearrangement.⁸ Carboryne can also insert into the α -C–H bond of dialkyl ethers.⁹ These findings suggest that carboryne has unique properties of its own, which is different from that of benzyne.⁵ As an ongoing project, we extended our research to include alkylbenzenes and report herein the reaction of carboryne with alkylbenzenes as well as the effects of alkyl substituents on the reactions.

RESULTS AND DISCUSSION

Reaction with Toluene. Heating a toluene solution of 1 at 110 °C overnight afforded two [4 + 2] cycloaddition isomers, 4a/4a', in a total yield of 44% with a molar ratio of 26/74. They were partially separated by flash column chromatography on

Received:February 16, 2012Published:March 26, 2012

silica gel. In addition, four minor products, **5a**, **6a**, **7a**, and **8a**, were also isolated from the product mixture in 10%, 6%, 6%, and 3% yields, respectively (Scheme 3). Compound **6a** was





easily characterized as 1-benzyl-*o*-carborane by comparison with the reported NMR data.¹⁰ Recrystallization of **5a**, **7a**, and **8a** from a mixture of hexane and ether led to single crystals suitable for X-ray analyses, and their structures are shown in Figures 1–3. Product **8a** was previously reported; however, no



Figure 1. Molecular structure of 5a. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.611(3), C(1)-C(11) = 1.587(3), C(2)-C(13) = 1.558(3), C(11)-C(12) = 1.555(3), C(12)-C(13) = 1.564(3), C(11)-C(16) = 1.541(3), C(13)-C(15) = 1.533(3), C(14)-C(15) = 1.506(3), C(14)-C(16) = 1.525(3), C(15)-C(16) = 1.536(3), C(12)-C(22) = 1.527(3), C(14)-C(21) = 1.497(3), C(21)-C(22) = 1.591(3).

NMR data are available.¹¹ It was noted that addition of AgF salt into the above reaction mixture produced no notable changes in the product distributions and yields.¹²

The formation of **5a** can be described as the result of homo-Diels–Alder reaction of the resulting [4 + 2] cycloadduct **4a'** with another equivalent of carboryne, similar to that observed in the corresponding benzyne reaction.^{1b} Interestingly, pyrolysis of the [4 + 2] cycloadduct **4a'** under vacuum also afforded the 2:1 adducts **5a** in 79% yield with the release of one equivalent of toluene (Scheme 4).¹³ Obviously, the [4 + 2]cycloadduct functions as both the donor^{4d} and the acceptor of the carboryne moiety under the reaction conditions. Moreover, the incoming carboryne selectively attacks the diene moiety of **4a'** from the unsubstituted side to avoid steric hindrance. A similar product, **5b**, was obtained via the pyrolysis of *tert*-butylsubstituted cycloadduct **4b** (Scheme 4). The structure of **5b** was also confirmed by single-crystal X-ray analyses (Figure 4).



Article

Figure 2. Molecular structure of 7a. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-C(2) = 1.610(4), C(1)-C(11) = 1.610(4), C(2)-C(12) = 1.550(4), C(11)-C(12) = 1.582(4), C(11)-C(17) = 1.545(4), C(11)-C(13) = 1.515(4), C(13)-C(14) = 1.322(4), C(14)-C(15) = 1.442(4), C(15)-C(16) = 1.314(4), C(16)-C(17) = 1.518(4), C(17)-C(21) = 1.552(4), C(21)-C(22) = 1.672(4); C(11)-C(1)-C(2) = 89.8(2), C(12)-C(2)-C(1) = 89.1(2), C(12)-C(11)-C(1) = 88.0(2), C(11)-C(12)-C(2) = 93.0(2).



Figure 3. Molecular structure of 8a. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.637(3), C(1)-C(11) = 1.488(3), C(2)-C(17) = 1.520(4), C(11)-C(16) = 1.386(3), C(16)-C(17) = 1.503(4).





1-Benzyl-*o*-carborane **6a** may result from the insertion of carboryne into the benzylic C–H bond,⁹ parallel with that of benzyne.^{1a}

The structure of 7a is strikingly informative, which can be regarded as an efficient capture of the reactive ene product 9aby carboryne in a [2 + 2] fashion (Scheme 3). In view of the formation of the rearomatized product *o*-benzylbiphenyl (Scheme 1),¹ it is very interesting that the dearomatized sixmembered ring in 9a is completely frozen in the molecular



Figure 4. Molecular structure of 5b. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.610(2), C(1)-C(11) = 1.569(2), C(2)-C(13) = 1.569(2), C(11)-C(12) = 1.555(2), C(12)-C(13) = 1.554(2), C(11)-C(15) = 1.527(2), C(13)-C(14) = 1.531(2), C(14)-C(15) = 1.530(2), C(14)-C(16) = 1.532(2), C(15)-C(16) = 1.532(2), C(12)-C(21) = 1.510(2), C(16)-C(22) = 1.535(2), C(21)-C(22) = 1.615(2).

structure of 7a, providing strong evidence for the existence of the ene reaction involving an aromatic double bond. The preference for the [2 + 2] cycloaddition on the terminal double bond is probably due to steric reasons.

The annulation product 8a is most likely to be another derivative of the reactive ene product 9a through a dehydrogenation reaction with another carboryne molecule.

Reaction with Alkylbenzenes. To investigate the substituent effects on the [4 + 2] cycloaddition reactions, various alkylbenzenes were treated with carboryne 2 to afford two isomers of Diels–Alder reaction as the major products in 35–67% isolated yields, as summarized in Table 1. The molecular structures of 4a, 4a', 4b, and 4c were determined by single-crystal X-ray analyses (Figures 5–8).

The observed isomeric ratio of 1,4- to 2,5-adduct seems to be confusing. However, after correction with statistical factors (that is, the observed regioselectivity being divided by the



Figure 5. Molecular structure of **4a**. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.599(2), C(1)-C(11) = 1.599(2), C(2)-C(15) = 1.579(2), C(11)-C(13) = 1.529(2), C(13)-C(14) = 1.317(2), C(14)-C(15) = 1.523(2), C(11)-C(16) = 1.531(2), C(16)-C(17) = 1.318(2), C(15)-C(17) = 1.526(2).

number of reactive sites in 3 for 1,4- or 2,5-addition in the [4 + 2] cycloaddition reaction), it is clear that steric factors play an important role in the regioselectivity of [4 + 2] cycloaddition reactions. When carboryne approaches the aromatic ring, there are two major steric repulsions, as shown in Scheme 5. One results from the interactions between the *ipso* carbon and the "fatty" cage in 1,4-addition fashion, and the other comes from the steric repulsions between the substituent R and the flanking cage B(3,6)-H hydrogen atoms in 2,5-addition fashion.¹⁴

For toluene and its derivatives 3a,d,e,f as well as trimethylsilylbenzene 3c, the corrected relative reactivities of 1,4- over 2,5-addition lie around 1, which indicates that the differences between the two types of steric interactions are small (Table 1, entries 1 and 3–6). On the other hand, remarkable differences were observed in the reactions of both *tert*-butylbenzene 3b and *p*-xylene 3g, as suggested by the corrected ratio of 1,4- over 2,5-adduct (Table 1, entries 2 and 7). It is noted that the reaction of benzyne with toluene or *tert*-

Table 1. Diels–Alder Reaction of Carboryne with	Alkylbenzenes
---	---------------

	$\frac{\mathbf{R}^{5}}{2}$	$ \begin{array}{c} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \\ \mathbf$	
entry	R'/R" (3)	$4 (\%)^a$	regioselectivity ^b (1,4-:2,5-)
1	Me/H (3a)	44	26:74 (41:59)
2	^t Bu/H (3b)	67	73:27 (84:16)
3	TMS/H (3c)	52	35:65 (51:49)
4 ^{<i>c</i>}	Me/6-Me (3d)	54	70:30 (54:46)
5	Me/3-Me (3e)	56	68:32 (52:48)
6 ^{<i>c</i>,<i>d</i>}	Me/3,4,6-Me ₃ (3f)	45	70:30 (54:46)
7	Me/4-Me (3g)	51	12:88 (21:79)
8^d	^t Bu/ ^t Bu (3h)	trace	
9	$Me/3,5-Me_2$ (3i)	65	
10^d	Me/2,3,4,5,6-Me ₅ (3j)	35	

^{*a*}Isolated yields. ^{*b*}Determined by ¹H NMR spectra of the crude product mixture. Ratios in parentheses refer to the selectivities corrected with statistical factors. Site refers to the reactive sites in 3. ^{*c*}Numbering inconsistent with IUPAC rules is adopted for differentiating 1,4- and 2,5-addition. ^{*d*}Using cyclohexane as the solvent.



Figure 6. Molecular structure of 4a'. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.596(3), C(1)-C(11) = 1.582(3), C(2)-C(15) = 1.578(3), C(11)-C(12) = 1.514(3), C(12)-C(13) = 1.320(3), C(13)-C(15) = 1.529(3), C(11)-C(16) = 1.515(3), C(16)-C(17) = 1.325(4), C(15)-C(17) = 1.511(3).



Figure 7. Molecular structure of 4b. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.610(3), C(1)-C(11) = 1.570(3), C(2)-C(14) = 1.639(3), C(11)-C(12) = 1.503(3), C(12)-C(13) = 1.319(3), C(13)-C(14) = 1.530(2), C(14)-C(15) = 1.566(3).

butylbenzene shows a similar regioselectivity.^{1a} Thus, the interactions between the bulky *tert*-butyl group and the axially flanking hydrogen atom in 2,5-addition fashion are seemingly very strong, which results in the unusual regioselectivity observed in the reaction of carboryne with **3b**. Such a phenomenon was not observed in the reaction of carboryne with **3c**, which can be ascribed to a much longer C–Si bond in **3c**, reducing significantly steric effects. On the other hand, in comparison to the favorable 2,5-addition observed in the reaction of carboryne with 1,4-di-*tert*-butylbenzene **3h** gave a trace amount of cycloadducts (Table 1, entry 8), because of the steric effects imposed by two *tert*-butyl groups. Steric factors were also reflected in the product yields, as shown in entries 9 and 10.

Reaction with Polycyclic Aromatics. Improved isolated yields were obtained from the reaction of **2** with polycyclic aromatics, as shown in Table 2. For anthracene, isopropyl ether was employed as the solvent, and the reaction was performed in the dark to suppress the reaction of carboryne with ether.⁹ In



Figure 8. Molecular structure of **4c**. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.608(2), C(1)-C(11) = 1.570(2), C(2)-C(14) = 1.602(2), C(11)-C(12) = 1.514(3), C(12)-C(13) = 1.317(3), C(13)-C(14) = 1.538(2), C(11)-C(15) = 1.514(3), C(15)-C(16) = 1.310(3), C(14)-C(16) = 1.539(2), Si(1)-C(14) = 1.914(2).





addition to the expected product 4l, a minor cycloadduct, 4l', was also isolated in ca. 4% yield, which was not observed before (Table 2, entry 2). Obviously, 9,10-addition of carboryne onto anthracene is electronically preferred. If the activated central aromatic ring is sterically blocked, the [4 + 2] cycloaddition on the less reactive aromatic ring in polycyclic aromatics proceeded, such as phenanthrene (Table 2, entry 3).

The molecular structures of **4l**' and **4m** were further confirmed by single-crystal X-ray analyses and are shown in Figures 9 and 10.

CONCLUSION

1-Iodo-2-lithiocarborane (1) is an efficient precursor to carboryne. It reacted with alkylbenzenes to give two regioisomers of the [4 + 2] cycloaddition reaction as the major products in moderate to good yields, in which the steric factors play an important role in the regioselectivity. Minor products derived from benzylic C-H insertion reaction, annulation reaction, tandem [4 + 2] cycloaddition/homo Diels-Alder reaction, and tandem ene reaction/[2 + 2] cycloaddition were also isolated and characterized in the reaction of carboryne with toluene. The presence of AgF in the above reaction produced no notable changes in the product distributions and yields. The observed [4 + 2] cycloaddition reactions are reversible, suggesting that the cycloadducts can



 Table 2. Diels-Alder Reaction of Carboryne with Polycyclic Aromatics

^{*a*}Ref 6b. ^{*b*}Performed in the dark in isopropyl ether. Isomeric ratio was determined by ¹H NMR spectrum of the crude product mixture.



Figure 9. Molecular structure of 4l'. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.598(4), C(1)-C(11) = 1.571(4), C(2)-C(14) = 1.573(4), C(11)-C(12) = 1.516(4), C(12)-C(13) = 1.317(4), C(13)-C(14) = 1.519(4), C(11)-C(15) = 1.523(4), C(15)-C(24) = 1.418(4), C(14)-C(24) = 1.520(4).

serve as carboryne source under pyrolysis conditions. This work also indicates that the differences in reactivities among carboryne and benzyne are mainly due to steric factors.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in flame-dried glassware under an atmosphere of dry N_2 or Ar with the rigid exclusion of air and moisture using standard Schlenk techniques unless



Figure 10. Molecular structure of 4m. All cage hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) = 1.603(2), C(1)-C(11) = 1.572(2), C(2)-C(14) = 1.578(2), C(11)-C(12) = 1.524(2), C(12)-C(13) = 1.319(2), C(13)-C(14) = 1.525(2), C(11)-C(15) = 1.524(2), C(15)-C(24) = 1.380(2), C(14)-C(24) = 1.526(2).

otherwise specified. All organic solvents were freshly distilled from Na-K alloy immediately prior to use. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. 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 a Bruker DPX 300 spectrometer at 96 MHz or a Varian Inova 400 spectrometer at 128 MHz. All signals were reported in ppm with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3 \cdot OEt_2$ (0.0 ppm) for boron chemical shifts. The data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad), coupling constant(s) in Hz, integration, and assignment. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Reaction of 2 with Toluene (3a). To a toluene solution (10 mL) of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ (1.0 mmol), prepared in situ from the reaction of "BuLi (1.25 mL, 1.6 M in hexane, 2.0 mmol) with *o*-carborane (144.2 mg, 1.0 mmol) at room temperature, was added iodine (253.8 mg, 1.0 mmol) at room temperature. After stirring at room temperature for 0.5 h, iodine completely disappeared and a white suspension was obtained. The reaction mixture was heated at 110 °C overnight and then quenched with wet *n*-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether. The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ¹H NMR spectroscopy and then subject to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane as eluent.

4a+4a': white solid (103.0 mg, 44%, 4a/4a' = 26/74). The two regioisomers, 4a and 4a', were partially separated in the pure form by flash column chromatography on silica gel (230-400 mesh) using nhexane as eluent. 4a: Colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.67 (t, *J* = 6.8 Hz, 2H), 6.37 (dd, *J* = 6.8, 1.2 Hz, 2H) (olefinic CH), 4.07 (t, J = 6.4 Hz, 1H) (CH), 1.64 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.5, 141.6, 81.5 (cage C), 79.1 (cage C), 50.3, 44.7, 19.2. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -1.7 (br, 4B), -12.2 (br, 6B). HRMS (EI): calcd for $C_9H_{16}^{11}B_8^{10}B_2^+$ 232.2250, found 232.2259. Anal. Calcd for $C_9H_{18}B_{10}$: C, 46.13; H, 7.74. Found: C, 46.14; H, 7.77. 4a': colorless crystals. ¹H NMR (400 MHz, CDCl₂): δ 6.67 (m, 2H), 6.22 (m, 1H) (olefinic CH), 4.03 (m, 1H), 3.78 (m, 1H) (CH), 1.87 (d, J = 1.6 Hz, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 150.5, 141.5, 140.0, 135.6, 79.5 (cage C), 76.8 (cage C), 49.9, 44.4, 19.8. ¹¹B{¹H} (96 MHz, CDCl₃): δ –1.8 (4B), –12.2 (6B). HRMS (EI): calcd for $C_9H_{16}^{11}B_8^{10}B_2^+$ 232.2250, found 232.2247.

5a: colorless crystals (18.8 mg, 10%). ¹H NMR (400 MHz, CDCl₃): δ 3.96 (s, 1H), 3.12 (s, 1H), 2.87 (s, 1H), 2.02 (d, J = 7.6 Hz, 1H), 1.68 (d, J = 7.6 Hz, 1H) (CH), 1.41 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 79.4 (cage C), 78.5 (cage C), 67.8 (cage C), 66.1 (cage C), 52.7, 52.6, 47.7, 35.8, 35.7, 33.9, 17.5. ¹¹B{¹H} (96 MHz, CDCl₃): δ 0.0 (2B), -2.3 (1B), -4.2 (2B), -9.7 (8B), -11.8 (7B). HRMS (EI): calcd for C₁₁H₂₆⁻¹¹B₁₆⁻¹⁰B₄⁺ ([M – 2H]⁺) 374.4035, found 374.4033.

6a:¹⁰ white powder (14.1 mg, 6%). ¹H NMR (400 MHz, acetoned₆): δ 7.36 (m, 3H), 7.27 (m, 2H) (aromatic CH), 4.51 (br, 1H) (cage CH), 3.69 (s, 2H) (CH₂). ¹¹B{¹H} (128 MHz, acetone-d₆): δ -1.6 (1B), -4.8 (1B), -8.4 (2B), -10.1 (2B), -10.9 (2B), -11.8 (2B).

7a: colorless crystals (11.3 mg, 6%). ¹H NMR (400 MHz, CDCl₃): δ 6.13 (m, 2H), 5.92 (d, J = 9.2 Hz, 1H), 5.77 (m, 1H) (olefinic CH), 3.95 (d, J = 6.4 Hz, 1H) (CH), 3.72 (d, J = 12.4 Hz, 1H) (CHH), 3.61 (br, 1H) (cage CH), 2.93 (d, J = 12.8 Hz, 1H) (CHH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 133.1, 126.4, 126.2, 125.1, 86.2 (cage C), 73.0 (cage C), 70.9 (cage C), 58.9 (cage C), 54.4, 46.8, 44.2. ¹¹B{¹H} (96 MHz, CDCl₃): δ -1.6 (2B), -3.1 (br, 3B), -10.6 (br, 15B). HRMS (EI): calcd for C₁₁H₂₈¹¹B₁₆¹⁰B₄⁺ 376.4192, found 376.4192.

8a: colorless crystals (7.3 mg, 3%). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 7.2, 1.6 Hz, 1H), 7.29 (m, 1H), 7.21 (d, J = 7.6 Hz, 1H) (aromatic CH), 3.69 (s, 2H) (CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.4, 138.6, 128.9, 127.8, 125.7, 121.4, 84.6 (cage C), 40.9, one cage carbon was not observed. ¹¹B{¹H} (128 MHz, CDCl₃): δ -6.6 (br, 4B), -8.7 (2B), -11.5 (2B), -12.8 (2B). This is a known compoud, ¹¹ but no NMR data were reported.

Pyrolysis of 4a'. A glass tube sealed with 4a' (46.8 mg, 0.2 mmol) under vacuum was heated at 250 °C for 4 h in a Muffle furnace. After cooling to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (230–400 mesh) using *n*-hexane/ether (*n*-hexane/ether = 100/1 in v/v) as eluent to give **5a** as colorless crystals (29.7 mg, 79%).

5b. This compound was prepared as colorless crystals from the pyrolysis of **4b** (55.3 mg, 0.2 mmol) using the same procedure reported for **5a**: 40.0 mg, 95%. ¹H NMR (400 MHz, CDCl₃): δ 3.85 (s, 1H), 3.04 (s, 2H), 1.51 (s, 2H) (CH), 1.14 (s, 9H) (C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 80.0 (cage C), 69.8 (cage C), 69.2 (cage C), 52.4, 50.2, 47.2, 37.2, 29.2, one cage carbon was not observed and the signal at 47.2 ppm may be assigned for two carbons. ¹¹B{¹H} (128 MHz, CDCl₃): δ -1.0 (2B), -2.9 (2B), -9.2 (5B), -10.4 (5B), -13.1 (6B). HRMS (EI): calcd for C₁₄H₃₃¹¹B₁₆¹⁰B₄⁺ ([M - H]⁺) 417.4583, found 417.4568.

Reactions of 2 with 3b–e, 3g, and 3i. These reactions were performed at a scale of 1.0 mmol of 2 using the same procedures reported for 3a.

4b+4**b**': white solid (185.7 mg, 67%, 4**b**/4**b**' = 73/27). 4**b** was obtained in pure form by recrystallization from hexane. 4**b**: colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.73 (t, *J* = 6.8 Hz, 2H), 6.65 (dd, *J* = 6.8, 1.6 Hz, 2H) (olefinic CH), 3.94 (m, 1H) (CH), 1.25 (br, 9H) (C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.1, 141.2, 82.1 (cage C), 80.6 (cage C), 64.5, 43.6, 34.9, 27.5 (br). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -1.5 (1B), -3.5 (3B), -11.1 (2B), -13.3 (2B), -14.2 (2B). HRMS (EI): calcd for C₁₂H₂₄¹¹B₈¹⁰B₂+ 276.2876, found 276.2874. Anal. Calcd for C₁₂H₂₄B₁₀: C, 52.14; H, 8.75. Found: C, 52.37; H, 8.59. 4**b**': The data were collected from the mixture of 4**b** and 4**b**', as it was unable to be isolated in pure form. ¹H NMR (400 MHz, CDCl₃): δ 6.66 (m, 2H), 6.15 (dd, *J* = 6.4, 2.0 Hz, 1H) (olefinic CH), 4.11 (m, 1H), 4.06 (m, 1H) (CH), 1.05 (s, 9H) (C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 161.7, 142.3, 141.2 (overlapped with one of 4**b**'s), 131.1, 78.7 (cage C), 46.0, 44.3, 34.2, 27.0, one cage carbon was not observed.

4c+4c': white solid (151.1 mg, 52%, **4c**/**4c**' = 35/65). Both **4c** and **4c**' were obtained in pure form by recrystallization from hexane. **4c**: colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.82 (t, *J* = 6.8 Hz, 2H), 6.53 (dd, *J* = 6.8, 1.2 Hz, 2H) (olefinic CH), 4.05 (t, *J* = 6.4 Hz, 1H) (CH), 0.25 (s, 9H) (Si(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.3, 143.6, 81.2 (cage C), 80.9 (cage C), 44.4, 44.3, -2.2. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -1.8 (1B), -2.3 (2B), -2.8

(1B), -11.9 (2B), -12.5 (4B). HRMS (EI): calcd for $C_{11}H_{24}Si^{11}B_8^{10}B_2^+$ 292.2652, found 292.2653. Anal. Calcd for $C_{11}H_{24}SiB_{10}$: C, 45.17; H, 8.27. Found: C, 45.10; H, 8.03. 4c': colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.85 (dd, *J* = 6.0, 1.2 Hz, 1H), 6.66 (m, 2H) (olefinic CH), 4.21 (dt, *J* = 5.6, 1.6 Hz, 1H), 4.17 (td, *J* = 6.0, 1.6 Hz, 1H) (CH), 0.13 (s, 9H) (Si(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 154.3, 149.6, 141.8, 140.8, 47.1, 45.5, -2.9, the cage carbons were not observed. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.1 (2B), -3.1 (2B), -12.4 (6B). HRMS (EI): calcd for $C_{11}H_{24}Si^{11}B_8^{10}B_2^+$ 292.2652, found 292.2659.

4d+4d': white solid (133.5 mg, 54%, **4d**/**4d**' = 70/30). **4d** was obtained in pure form by recrystallization from hexane. **4d**: colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.66 (t, *J* = 6.8 Hz, 1H), 6.29 (m, 2H) (olefinic CH), 3.93 (m, 1H) (CH), 1.79 (d, *J* = 1.2 Hz, 3H), 1.55 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.6, 146.3, 141.3, 137.7, 81.4 (cage C), 80.7 (cage C), 52.5, 43.9, 17.2, 16.6. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -1.2 (4B), -11.6 (6B). HRMS (EI): calcd for C₁₀H₂₀¹¹B₈¹⁰B₂⁺ 248.2563, found 248.2553. Anal. Calcd for C₁₀H₂₀B₁₀: C, 48.36; H, 8.12. Found: C, 48.37; H, 8.13. **4d**': The data were collected from the mixture of **4d** and **4d**', as it was unable to be isolated in pure form. ¹H NMR (400 MHz, CDCl₃): δ 6.66 (m, 2H) (olefinic CH), 3.76 (br, 2H) (CH), 1.72 (s, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.5, 140.1, 79.0 (cage C), 50.3, 16.8.

4e+4e': white solid (139.8 mg, 56%, **4e/4e'** = 68/32). **4e** was obtained in pure form by recrystallization from hexane. **4e**: colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.64 (t, *J* = 6.8 Hz, 1H), 6.36 (dd, *J* = 6.8, 1.2 Hz, 1H), 5.90 (s, 1H) (olefinic CH), 3.71 (dt, *J* = 6.0, 1.2 Hz, 1H) (CH), 1.86 (d, *J* = 1.6 Hz, 3H), 1.60 (s, 3H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 150.8, 146.7, 141.0, 140.3, 83.7 (cage C), 78.7 (cage C), 50.0, 49.8, 19.7, 19.3. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -1.3 (4B), -11.7 (6B). HRMS (EI): calcd for C₁₀H₂₀¹¹B₈¹⁰B₂+ 248.2563, found 248.2554. Anal. Calcd for C₁₀H₂₀B₁₀: C, 48.36; H, 8.12. Found: C, 48.34; H, 8.33. **4e'**: The data were collected from the mixture of **4e** and **4e'**, as it was unable to be isolated in pure form. ¹H NMR (400 MHz, CDCl₃): δ 6.22 (dt, *J* = 6.4, 1.6 Hz, 2H) (olefinic CH), 3.91 (t, *J* = 6.4 Hz, 1H), 3.46 (t, *J* = 1.6 Hz, 1H) (CH), 1.88 (d, *J* = 2.0 Hz, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.2, 135.9, 81.7 (cage C), 76.5 (cage C), 55.1, 44.1, 19.9.

4g+**4g**': white solid (125.9 mg, 51%, **4g**/**4g**' = 12/88). **4g**' was obtained in pure form by recrystallization from hexane. **4g**: The data were collected from the mixture of **4g** and **4g**', as it was unable to be isolated in pure form. ¹H NMR (400 MHz, CDCl₃): δ 6.34 (s, 4H) (olefinic CH), 1.61 (s, 6H) (CH₃). **4g**': colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.19 (dt, *J* = 6.4, 2.0 Hz, 2H) (olefinic CH), 3.67 (dd, *J* = 6.4, 2.0 Hz, 2H) (CH), 1.87 (d, *J* = 1.6 Hz, 6H) (CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 150.9, 134.4, 79.1 (cage C), 49.6, 19.8. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -1.9 (1B), -5.0 (1B), -8.3 (2B), -9.9 (2B), -12.4 (4B). HRMS (EI): calcd for C₁₀H₂₀¹¹B₈¹⁰B₂+ 248.2563, found 248.2555. Anal. Calcd for C₁₀H₂₀B₁₀: C, 48.36; H, 8.12. Found: C, 48.38; H, 8.22.

4i: colorless crystals (169.5 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ 5.90 (s, 2H) (olefinic CH), 3.38 (t, J = 1.6 Hz, 1H) (CH), 1.86 (d, J = 1.6 Hz, 6H), 1.55 (s, 3H) (CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 149.6, 141.2, 85.8 (cage C), 78.3 (cage C), 55.1, 49.7, 19.9, 19.3. ¹¹B{¹H} NMR (96 MHz, CDCl₃): δ -1.6 (4B), -12.0 (6B). HRMS (EI): calcd for C₁₁H₂₂H₈¹⁰B₂⁺ 262.2719, found 262.2711. Anal. Calcd for C₁₁H₂₂B₁₀: C, 50.35; H, 8.45. Found: C, 50.08; H, 8.58.

Reaction of 2 with 3f. To an in situ prepared cyclohexane solution (10 mL) of **1** (1.0 mmol) at room temperature was added **3f** (147.6 mg, 1.1 mmol). The reaction mixture was heated at 110 °C overnight and then quenched with wet *n*-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether. The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ¹H NMR spectroscopy and then subject to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane as eluent to give **4f**+**4f'** as a white solid (124.0 mg, 45%, **4f**/**4f'** = 70/30). Both **4f** and **4f'** were obtained in pure form by recrystallization from hexane. **4f**: colorless crystals. ¹H NMR (400

MHz, CDCl₃): δ 5.90 (d, J = 1.2 Hz, 2H) (olefinic CH), 1.76 (d, J = 2.0 Hz, 6H), 1.48 (s, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.7, 142.9, 84.9 (cage C), 51.3, 17.4, 16.5. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.3 (4B), -13.0 (6B). HRMS (EI): calcd for C₁₂H₂₄¹¹B₈¹⁰B₂⁺ 276.2876, found 276.2864. Anal. Calcd for C₁₂H₂₄B₁₀: C, 52.14; H, 8.75. Found: C, 52.31; H, 8.64. **4f**': colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 3.39 (s, 2H) (CH), 1.73 (s, 12H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.5, 80.7 (cage C), 56.1, 16.8. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.5 (4B), -12.8 (6B). HRMS (EI): calcd for C₁₂H₂₄¹¹B₈¹⁰B₂⁺ 276.2876, found 276.2865.

Reactions of 2 with 3h, 3j, 3k, and 3m. These reactions were performed at a scale of 1.0 mmol of 2 using the same procedures reported for 3f.

4j: colorless crystals (106.5 mg, 35%). ¹H NMR (400 MHz, CDCl₃): δ 1.64 (s, 12H), 1.48 (s, 6H) (CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.6, 85.7 (cage C), 52.7, 16.8, 13.9. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.7 (4B), -13.5 (6B). HRMS (EI): calcd for C₁₄H₂₈¹¹B₈¹⁰B₂⁺ 304.3189, found 304.3184. Anal. Calcd for C₁₄H₂₈B₁₀: C, 55.22; H, 9.27. Found: C, 55.17; H, 9.08.

4k:^{6b} colorless crystals (163.3 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ 7.12 (m, 4H) (aromatic CH), 6.83 (m, 2H) (olefinic CH), 4.40 (m, 2H). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.0 (2B), -4.4 (2B), -11.0 (2B), -12.7 (4B).

4m: colorless crystals (80.7 mg, 25%). ¹H NMR (400 MHz, CDCl₃): *δ* 7.97 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.56 (m, 1H), 7.48 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 1H) (aromatic CH), 7.00 (m, 1H), 6.95 (m, 1H) (olefinic CH), 5.25 (dd, *J* = 6.4, 1.2 Hz, 1H), 4.60 (dd, *J* = 6.4, 1.6 Hz, 1H) (CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): *δ* 144.1, 142.5, 141.8, 140.7, 132.1, 128.9, 128.4, 127.2, 127.0, 126.1, 122.3, 121.7, 78.8 (cage C), 78.5 (cage C), 48.5, 43.2. ¹¹B{¹H} NMR (128 MHz, CDCl₃): *δ* -2.0 (2B), -3.6 (br, 2B), -11.4 (2B), -12.5 (4B). HRMS (EI): calcd for C₁₆H₂₀¹¹B₈¹⁰B₂⁺: 320.2570, found 320.2573.

Reaction of 2 with 3l. To a diisopropyl ether solution (10 mL) of $1,2-Li_2-C_2B_{10}H_{10}$ (1.0 mmol) in the dark (covered with aluminum foil), prepared in situ from the reaction of "BuLi (1.25 mL, 1.6 M in hexane, 2.0 mmol) with o-carborane (144.2 mg, 1.0 mmol) in an icewater bath, was added iodine (253.8 mg, 1.0 mmol). After stirring at 0 °C for 0.5 h, iodine completely disappeared and a white suspension was obtained. To this suspension was added 31 (195.8 mg, 1.1 mmol). The reaction mixture was heated at 110 °C overnight in the dark and then quenched with wet n-hexane. The resulting suspension was quickly passed through a short column of silica gel to remove the inorganic salts and washed with ether. The organic portions were combined. After removal of solvents in vacuo, the residue was analyzed by ¹H NMR spectroscopy and then subject to flash column chromatography on silica gel (230-400 mesh) using n-hexane as eluent to give 4l and 4l' as a white solid (4l: 193.2 mg, 60%; 4l': 12.9 mg, 4%; 4l/4l' = 94/6). 4l:^{6b} ¹H NMR (400 MHz, CDCl₃): δ 7.22 (m, 4H), 7.17 (m, 4H) (aromatic CH), 4.75 (s, 2H) (CH). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -2.1 (2B), -5.3 (br, 2B), -11.6 (4B), -12.5 (2B). 4l': ¹H NMR (400 MHz, CDCl₃): δ 7.75 (m, 2H), 7.49 (m, 4H) (aromatic CH), 6.83 (m, 2H) (olefinic CH), 4.48 (m, 2H) (CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.2, 139.6, 131.8, 128.0, 126.9, 122.1, 77.7 (cage C), 47.3. ¹¹B{¹H} NMR (128 MHz, CDCl₂): $\delta - 2.2$ (2B), -5.8 (br, 2B), -10.7 (2B), -12.8 (br, 4B). HRMS (EI): calcd for $C_{16}H_{20}^{-11}B_8^{-10}B_2^{+}$ 320.2570, found 320.2561.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program.¹⁵ 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 on F^2 using the SHELXTL program package.¹⁶ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Table S1 in the Supporting Information. Further details are also included in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra of all new compounds and crystallographic data in CIF format for 4a, 4a', 4b, 4c, 4l', 4m, 5a, 5b, 7a, and 8a. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zxie@cuhk.edu.hk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. 404011), National Basic Research Program of China (973 Program) (Project No. 2012CB821600), and NSFC/RGC Joint Research Scheme (No. N_CUHK470/10). We thank Ms. Hoi-Shan Chan for single-crystal X-ray analyses.

REFERENCES

(1) (a) Brinkley, J. M.; Friedman, L. Tetrahedron Lett. 1972, 13, 4141-4142. (b) Tabushi, I.; Yamda, H.; Yoshida, Z.; Oda, R. Bull. Chem. Soc. Jpn. 1977, 50, 285-290.

(2) (a) Miller, R. G.; Stiles, M. J. Am. Chem. Soc. 1963, 85, 1798– 1800. (b) Stiles, M.; Burckhardt, U.; Freund, G. J. Org. Chem. 1967, 32, 3718–3719. (c) Friedman, L. J. Am. Chem. Soc. 1967, 89, 3071– 3073. (d) Tabushi, I.; Yamda, H.; Yoshida, Z.; Oda, R. Bull. Chem. Soc. Jpn. 1977, 50, 291–296.

(3) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M. Jr. J. Am. Chem. Soc. 1990, 112, 4082–4083.

(4) (a) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M. Jr. J. Am. Chem. Soc. 1991, 113, 1313–1318. (b) Gingrich, H. L.; Ghosh, T.; Huang, Q.; Li, J.; Jones, M. Jr. Pure Appl. Chem. 1993, 65, 65–71. (c) Barnett-Thamattoor, L.; Zheng, G.-X.; Ho, D. M.; Jones, M. Jr.; Jackson, J. E. Inorg. Chem. 1996, 35, 7311–7315. (d) Atkins, J. H.; Ho, D. M.; Jones, M. Jr. Tetrahedron Lett. 1996, 37, 7217–7220. (e) Wang, S. R.; Xie, Z. Tetrahedron 2012, DOI: 10.1016/ j.tet.2012.02.049.

(5) (a) Hoffmann, R. W. Dehydrobenzene and Cycloalkynes; Academic: New York, 1967. (b) Pellissier, H.; Santelli, M. Tetrahedron 2003, 59, 701–730.

(6) (a) Jeon, J.; Kitamura, T.; Yoo, B.-W.; Kang, S. O.; Ko, J. *Chem. Commun.* **2001**, 2110–2111. (b) 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.

(7) Qiu, Z.; Wang, S. R.; Xie, Z. Angew. Chem., Int. Ed. 2010, 49, 4649–4652.

(8) Wang, S. R.; Qiu, Z.; Xie, Z. J. Am. Chem. Soc. 2010, 132, 9988–9989.

(9) Wang, S. R.; Qiu, Z.; Xie, Z. J. Am. Chem. Soc. 2011, 133, 5760–5763.

(10) Armstrong, A. F.; Valliant, J. F. Inorg. Chem. 2007, 46, 2148–2158.

(11) Zakharkin, L. I.; Chapovskii, Yu. A.; Brattsev, V. A.; Stanko, V. I. *Zh. Obshch. Khim.* **1966**, *36*, 878–886.

(12) For metal-carboryne chemistry, see: (a) Deng, L.; Chan, H.-S.; Xie, Z. J. Am. Chem. Soc. 2005, 127, 13774-13775. (b) Deng, L.; Chan, H.-S.; Xie, Z. J. Am. Chem. Soc. 2006, 128, 7728-7729. (c) Qiu, Z.; Xie, Z. Angew. Chem., Int. Ed. 2008, 47, 6572-6575. (d) Qiu, Z.; Xie, Z. J. Am. Chem. Soc. 2009, 131, 2084-2085. (e) Ren, S.; Chan, H.-S.; Xie, Z. J. Am. Chem. Soc. 2009, 131, 3862-3863. (f) Qiu, Z.; Xie, Z. J. Am. Chem. Soc. 2010, 132, 16085-16093. (g) Ren, S.; Qiu, Z.; Xie, Z. Angew. Chem., Int. Ed. 2012, 51, 1010-1013. (h) Ren, S.; Qiu, Z.; Xie, Z. J. Am. Chem. Soc. 2012, 134, 3242–3254. (i) Qiu, Z.; Ren, S.; Xie, Z. Acc. Chem. Res. 2011, 44, 299–309.

(13) Pyrolysis of benzobicyclo[2.2.2]octatriene in benzene- d_6 was reported to afford only naphthalene and biphenyl; see: Friedman, L.; Lindow, D. F. J. Am. Chem. Soc. **1968**, 90, 2329–2333.

(14) Gingrich, H. L.; Huang, Q.; Morales, A. L.; Jones, M. Jr. J. Org. Chem. 1992, 57, 3803-3806.

(15) Sheldrick, G. M. SADABS: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

(16) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, USA, 1997.