

Reduction of 1,2-(CH₂)_n-1,2-C₂B₁₀H₁₀ by Group 1 Metals. Effects of Bridge Length/Rigidity on the Formation of Carborane Anions

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Received August 6, 2005

The effects of bridge length and rigidity on the formation of C,C'-linked carborane anions were studied. Reaction of 1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀ (**1**), 1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀ (**2**), or 1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀ (**3**) with excess Li metal in THF gave "carbon-atoms-adjacent" (CA_d) *arachno*-carborane salt [1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**6**), [1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**7**), or [1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**8**), respectively. On the other hand, reduction of 1,2-(CH₂)₅-1,2-C₂B₁₀H₁₀ (**4**) or 1,2-(CH₂)₆-1,2-C₂B₁₀H₁₀ (**5**) with excess Li metal followed by cation exchange of NaI, or directly with excess Na metal, afforded "carbon-atoms-apart" (CA_p) *nido*-carborane salt [1,3-(CH₂)₅-1,3-C₂B₁₀H₁₀]{Na₂(THF)₄}]_n (**9**) or [1,4-(CH₂)₆-1,4-C₂B₁₀H₁₀]{Na₂(THF)₄}]_n (**10**). All complexes were fully characterized by various spectroscopic techniques and elemental analyses as well as single-crystal X-ray diffraction studies. The results showed that although both the bridge length and rigidity of C,C'-linked *o*-carboranes have significant effects on the formation of carborane anions, the former plays a more important role than the latter in controlling the relative positions of the two cage carbon atoms during the reductive process.

Introduction

It is well established that the reduction of *o*-R₂C₂B₁₀H₁₀ by group 1 metals always results in the complete cleavage of the cage carbon-carbon bond, leading to the formation of "carbon-atoms-apart" (CA_p) *nido*-carborane dianions [7,9-*nido*-R₂C₂B₁₀H₁₀]²⁻ (*meta* in Chart 1).¹ They are very useful ligands for the production of numerous metallocarboranes of s, p, d, and f elements.^{2,3} We recently developed a method to control the relative positions of the cage carbon atoms during the reduction process by introducing a bridge between the two cage

Chart 1. *nido*-C₂B₁₀H₁₂²⁻ Isomers



carbon atoms.⁴ Thus the syntheses of "carbon-atoms-adjacent" *nido*-carborane dianions (CA_d) [7,8-*nido*-R₂C₂B₁₀H₁₀]²⁻ (*ortho* in Chart 1) and CA_p [7,10-*nido*-R₂C₂B₁₀H₁₀]²⁻ (*para* in Chart 1) were achieved.⁴ The results showed that a short bridge can not only lock the cage carbon atoms in *ortho* positions but also lower the reducing power of the resulting dianions, leading to the formation of CA_d [*arachno*-R₂C₂B₁₀H₁₀]⁴⁻ by further reduction with Li metal.⁴

These CA_d *nido*- and *arachno*-carborane anions are interesting ligands to transition metals.⁵ Most importantly, they are finding applications in the preparation of 13- and 14-vertex supracarboranes. For examples, Welch's group reported the synthesis of a 13-vertex carborane 1,2-C₆H₄(CH₂)₂-3-Ph-1,2-C₂B₁₁H₁₀ using the CA_d [*nido*-1,2-C₆H₄(CH₂)₂-1,2-C₂B₁₀H₁₀]²⁻ as the starting material,⁶ we prepared a 14-vertex carborane 1,2-(CH₂)₃-1,2-C₂B₁₂H₁₂ from CA_d [*arachno*-1,2-(CH₂)₃-1,2-

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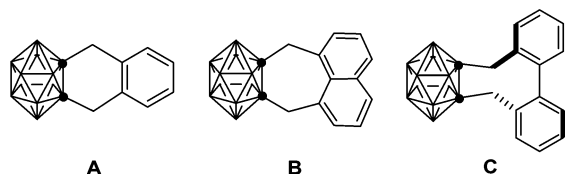
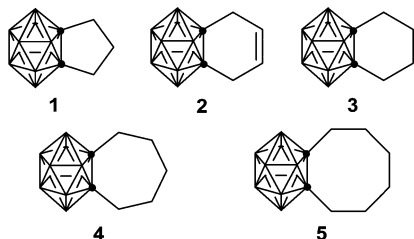
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Chart 2. *o*-Carboranes with Aromatic BridgesChart 3. *o*-Carboranes with Aliphatic Bridges

C₂B₁₀H₁₀].^{4–7} We also examined the reaction of CAD [*arachno*-1,2-C₆H₄(CH₂)₂-1,2-C₂B₁₀H₁₀]^{4–} with borane dihalides, from which only 13-vertex carboranes were isolated and no 14-vertex carboranes were detected. These results indicated that the bridges are both electronically and sterically important to these capping reactions.

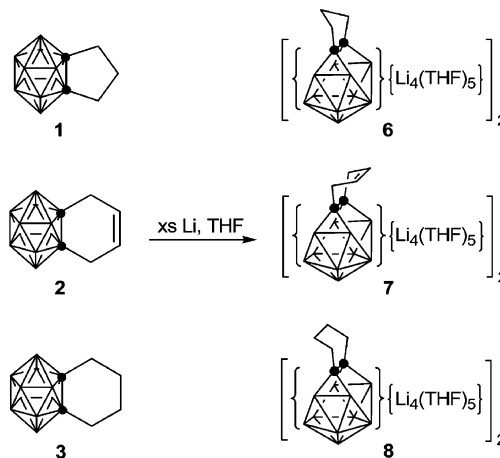
Our earlier study on the reactions of 1,2-Ar(CH₂)₂-1,2-C₂B₁₀H₁₀ (Chart 2) with group 1 metals showed that the aromatic bridges have significant effects on the formation of carborane anions.⁴ However, the rigidity of these bridges made the conclusions ambiguous. Which factor (bridge length or rigidity) plays a more important role in controlling the positions of the cage carbon atoms during the reduction process? In this connection, we extended our research to include *o*-carboranes with aliphatic bridges, 1,2-(CH₂)_n-1,2-C₂B₁₀H₁₀ (*n* = 3–6) (Chart 3), and report here their reactions with group 1 metals.⁸ Differences and similarities among carboranes with aromatic and aliphatic bridges in the reduction reactions are also discussed in this article.

Results and Discussion

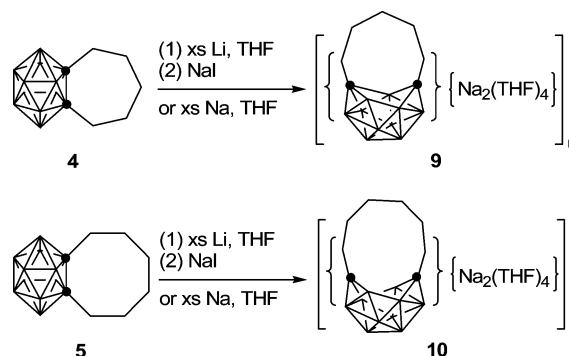
Reduction with Group 1 Metals. Compounds 1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀ (**1**),⁹ 1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀ (**2**),¹⁰ 1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀ (**3**),⁹ and 1,2-(CH₂)₅-1,2-C₂B₁₀H₁₀ (**4**)⁹ were prepared according to the literature methods. Compound 1,2-(CH₂)₆-1,2-C₂B₁₀H₁₀ (**5**) was prepared in 17% yield from the reaction of Li₂C₂B₁₀H₁₀ with 1,6-dibromohexane in toluene/Et₂O (2: 1, v/v). The low yield was probably due to the formation of insoluble oligomers/polymers by intermolecular coupling reactions. Compounds **1–5** bear a five-, six-, seven-, and eight-membered ring, respectively, constructed by the two cage carbon atoms and aliphatic chains, which enable us to investigate the relationships between the bridge length/rigidity and the relative positions of the cage carbon atoms in the reduction reactions.

Treatment of **1–3** with excess finely cut lithium metal in THF at room temperature gave CAD *arachno*

Scheme 1



Scheme 2



species [**1,2**-(CH₂)₃-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**6**), [**1,2**-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**7**), and [**1,2**-(CH₂)₄-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅}]₂ (**8**) in ~85% yield, respectively (Scheme 1). They were crystallized out nicely as colorless crystals from THF solutions. On the other hand, the reaction of **4** or **5** with excess lithium metal in THF afforded only CAP *nido*-carborane salt [1,3-(CH₂)₅-1,3-C₂B₁₀H₁₀]{Li₂(THF)_x} or [1,4-(CH₂)₆-1,4-C₂B₁₀H₁₀]{Li₂(THF)_x} as a sticky solid, subsequently followed by the cation exchange with NaI in THF, producing [**1,3**-(CH₂)₅-1,3-C₂B₁₀H₁₀]{Na₂(THF)₄}]_n (**9**) or [**1,4**-(CH₂)₆-1,4-C₂B₁₀H₁₀]{Na₂(THF)₄}]_n (**10**) as colorless crystals in ~70% yield. Complexes **9** and **10** were also prepared in 77% and 80% yields from the reactions of **4** and **5** with finely cut sodium metal in THF, respectively (Scheme 2). It was noted that naphthalene was not required for the above reactions. These reactions were closely monitored by the ¹¹B NMR techniques since *closo*-, *nido*-, and *arachno*-carboranes have distinct ¹¹B NMR spectra.

Complexes **6–10** were extremely air- and moisture-sensitive, but remained stable for months at room temperature under an inert atmosphere. They were soluble in pyridine and THF and insoluble in toluene and *n*-hexane.

The methylene protons of the bridges were observed in the ¹H NMR spectra of **6–10** in the range δ 3.02–1.65 ppm. In addition, two olefinic protons were also observed at δ 5.80 and 6.93 ppm, respectively, in the ¹H NMR spectrum of **7**. The ¹H NMR spectra supported a ratio of five THF molecules per carboranyl for **6**, **7**, and **8** and four THF molecules per carboranyl for **9** and **10**. The ¹³C NMR spectra of these complexes were

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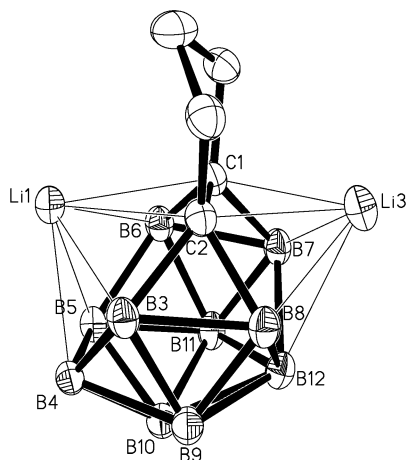
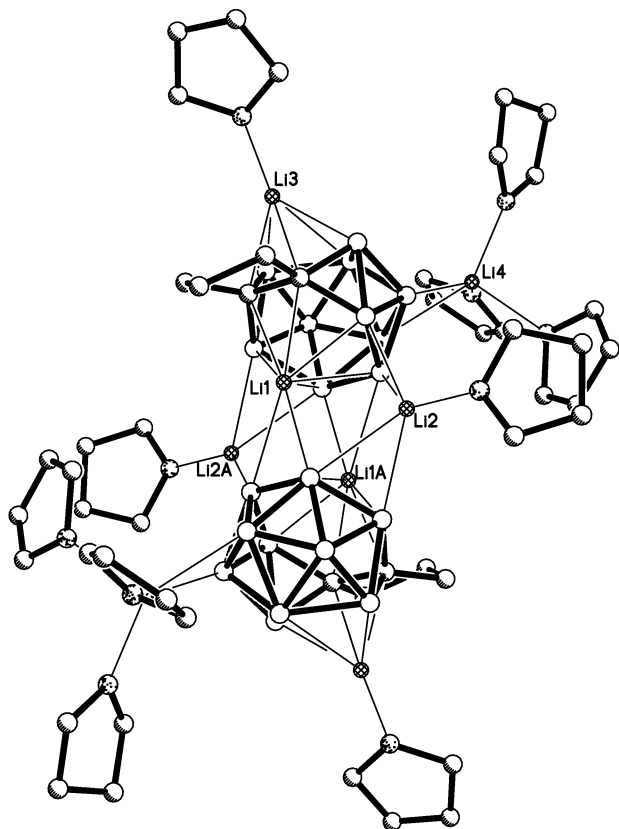


Figure 1. Top: molecular structure of $[\{1,2-(\text{CH}_2)_3-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_5]_2$ (**6**). Bottom: bonding interactions between Li^+ and open faces.

consistent with their ^1H NMR data. The ^{11}B NMR spectra exhibited a 2:2:3:1:1:1, 2:2:3:1:2, or 4:2:1:3 splitting pattern for **6**, **7**, or **8** and a 2:2:4:2 splitting pattern for both **9** and **10**. Their solid-state IR spectra displayed a very strong broad peak and a medium strong one in the range $2300\text{--}2500\text{ cm}^{-1}$, characteristic of B–H–M interactions.

Molecular Structures of 6–8. Single-crystal X-ray analyses revealed that **6** (Figure 1), **7** (Figure 2), and **8** (Figure 3) are centrosymmetric dimers having similar solid-state structures. They contain a structural

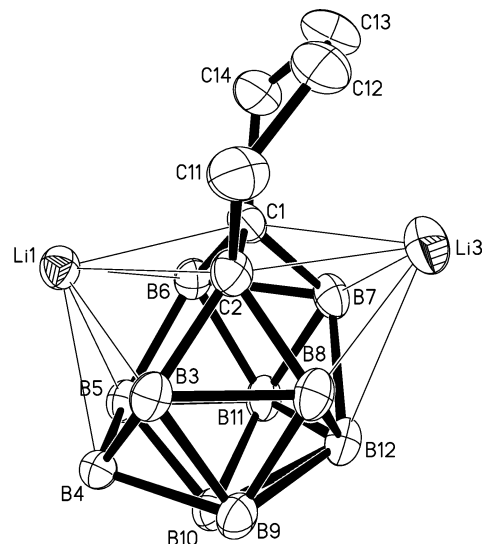


Figure 2. Bonding interactions between Li^+ and open faces in $[\{1,2-(\text{CH}_2\text{CH}=\text{CHCH}_2)-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_5]_2$ (**7**).

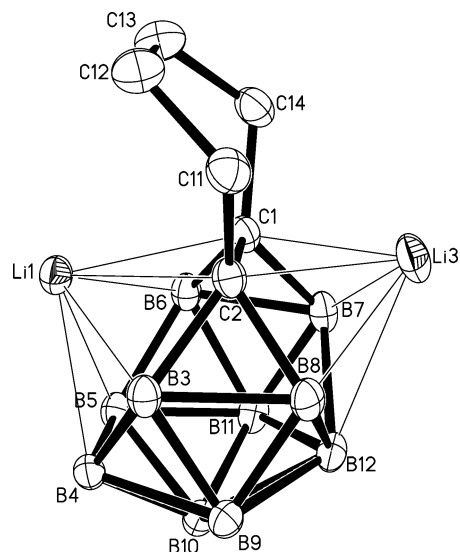
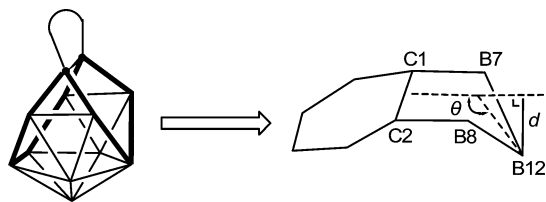


Figure 3. Bonding interactions between Li^+ and open faces in $[\{1,2-(\text{CH}_2)_4-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}\text{Li}_4(\text{THF})_5]_2$ (**8**).

motif of the *arachno*-carborane bearing one open six-membered face and one open five-membered face that are bonded to two lithium atoms in η^6 - and η^5 -fashion, respectively, forming a 14-vertex metallocarborane unit.¹¹ These two open faces share one common edge of C(1)–C(2). The atoms in the C_2B_4 face are almost coplanar, whereas the C_2B_3 faces are bent with dihedral angles of $\sim 151^\circ$.

As shown in Table 1, the average Li(1)–cage atom (C_2B_4 face) and Li(3)–cage atom (C_2B_3 face) distances of 2.298(6) and 2.257(6) Å in **6** are very close to the corresponding values of 2.301(6) and 2.254(6) Å in **8**. Those of 2.298(9) and 2.314(10) Å in **7** are very comparable to the corresponding values of 2.315(8) and 2.309(10) Å found in $[\{1,2-\text{C}_6\text{H}_4(\text{CH}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}$

(11) For 14-vertex metallocarboranes; see ref 4a and: (a) Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 38. (b) Maxwell, W. M.; Bryan, R. F.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4016. (c) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 6. (d) Ellis, D.; Lopez, M. E.; McIntosh, R.; Rosair, G. M.; Welch, A. J. *Chem. Commun.* **2005**, 1917.

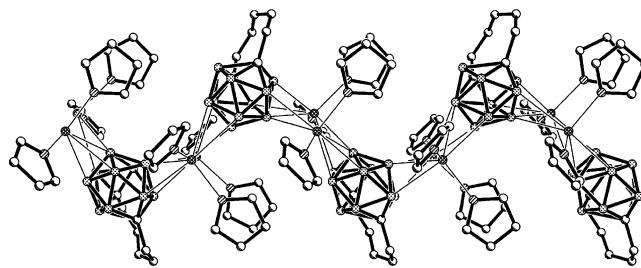
Table 1. Selected Structural Data for CAd arachno-Carborane Anions^a

	6	11^b	7	8
C(1)–C(2)	1.560(4)	1.562(4)	1.568(6)	1.579(4)
B(7)···B(8)	2.776(5)	2.726(6)	2.686(8)	2.744(5)
Li(3)–B(12)	2.628(6)	2.572(9)	2.697(10)	2.638(6)
av Li(1)–cage atom	2.298(6)	2.315(8)	2.298(9)	2.301(6)
av Li(3)–cage atom	2.257(6)	2.309(10)	2.314(10)	2.254(6)
<i>d</i>	0.632	0.603	0.624	0.617
θ	150.6	151.6	151.3	151.3

^a Distances are in Å and angles are in deg. ^b [$\{1,2\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}\}\{\text{Li}_4(\text{THF})_6\}_2$ (**11**); see ref 4a.

$\{\text{Li}_4(\text{THF})_6\}_2$ (**11**).^{4a} The much longer Li(3)–cage atom distances observed in **7** and **11** may result from the interactions between the Li(3) and the C=C double bond of the bridges. It is noted that the Li(3)–B(12) distances of 2.628(6) Å in **6**, 2.697(10) Å in **7**, and 2.638(6) Å in **8** are significantly longer than the other Li–cage atom distances due to the large out-of-plane (C(1)C(2)B(7)B(8) plane) displacement of B(12), 0.632 Å in **6**, 0.624 Å in **7**, and 0.617 Å in **8**, respectively. The most notable difference among these structures is the folding direction of the bridges. The CH₂CH=CHCH₂ bridge in **7** folds toward the C₂B₃ face, whereas the (CH₂)₃ and (CH₂)₄ ones in **6** and **8** point toward the C₂B₄ face, most likely due to the interactions between the C=C bond and Li(3) atom in **7** (2.577(11) and 2.613(11) Å). Such interactions were also observed in **11**, forcing the C₆H₄(CH₂)₂ moiety to fold toward the C₂B₃ face.^{4a} In this regard, the structure of **7** is closer to that of **11**, rather than **6** and **8**. This difference might be meaningful to the reactions of CAd arachno-carborane salts with borane dihalides because the redox and capitation are two competitive reactions in this system. At least, these structural data provide useful information for the capitation step in the preparation of supracarboranes.^{6,7}

Molecular Structures of 9 and 10. An X-ray analysis revealed that complex **9** adopts a polymeric structure in which the sodium atom and the *nido*-1,3-carborane serve as alternating linkages to give a zigzag carborane–Na–carborane–Na infinite chain, which is maintained in one dimension throughout the lattice (Figure 4). This novel [*nido*-1,3-(CH₂)₅-1,3-C₂B₁₀H₁₀]²⁻ dianion represents a new member of the *nido*-R₂C₂B₁₀H₁₀²⁻ family. The cage C(1)···C(2) and C(2)···B(6) connectivities are broken during the reductive process, leading to the formation of a highly distorted five-membered C₂B₃ face with an elongated C(1)–B(3) bond. The key structural data are compiled in Table 2 for comparison. C(2) is a typical four-coordinate carbon, whereas C(1) is best described as a five-coordinate one. The formation of this unique structure may result from the contrary effects of the ring constraint and the repulsion between the two negatively charged cage carbon atoms.

**Figure 4.** Top: infinite polymeric chain of [$\{1,3\text{-(CH}_2)_5\text{-1,3-C}_2\text{B}_{10}\text{H}_{10}\}\text{Na}_2(\text{THF})_4\}_n$ (**9**). Bottom: structure of the anion in **9**.**Table 2. Selected Distances (Å) for CAd nido-Carborane Anions**

	C(1)···C(2)	C(1)···B(3)	C(2)···B(6)
9	2.687(6)	2.083(8)	2.302(9)
12^a	2.836(4)	2.553(7)	2.528(10)
10	2.872(7)	2.594(5)	2.594(13)

^a [$\{\mu\text{-1,4-[1,1'-(C}_6\text{H}_4)_2\text{-2,2'-(CH}_2)_2\text{-1,4-C}_2\text{B}_{10}\text{H}_{10}\}\{\text{Na}_2(\text{THF})_3\}_n$ (**12**); see ref 4c.

Single-crystal X-ray diffraction studies confirmed that **10** is also a one-dimensional coordination polymer, like **9**. As the ring size increases by one methylene unit, the C(1)–B(3) distance is forced to be further separated, generating a highly distorted six-membered C₂B₄ face, shown in Figure 5. The C(1)···C(2) and C(2)···B(6) separations are also increased on going from **9** to **10** due to the ring size effect. The structural parameters of the *nido*-carborane cage in **10** are close to those observed in [$\{\mu\text{-1,4-[1,1'-(C}_6\text{H}_4)_2\text{-2,2'-(CH}_2)_2\text{-1,4-C}_2\text{B}_{10}\text{H}_{10}\}\{\text{Na}_2(\text{THF})_3\}_n$ (**12**),^{4c} as shown in Table 2. These data suggest that the overall ring forces of the (CH₂)₆ and 1,1'-(C₆H₄)₂-2,2'-(CH₂)₂ units acting on the cage are

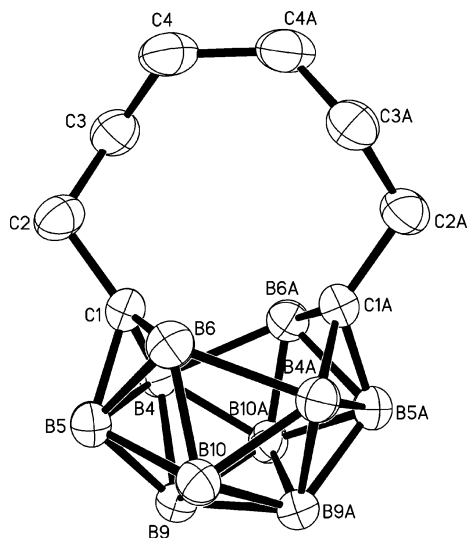


Figure 5. Structure of the anion in $[\{1,4-(\text{CH}_2)_6-1,3-\text{C}_2\text{B}_{10}\text{H}_{10}\}\text{Na}_2(\text{THF})_4]_n$ (**10**).

similar, although the rigidity of the bridges is quite different.

Comparing the reductions of **A–C** in Chart 2⁴ and **1–5** in Chart 3 with group 1 metals, significant difference was observed in the seven-membered ring system. The CAd carborane anions were obtained from **B**, whereas only the CAp carborane dianion was generated from **4**, indicating the importance of the bridge rigidity in this system.

Conclusion

This work shows that although both the length and rigidity of the bridges in C,C'-linked *o*-carboranes have significant effects on the formation of carborane anions, the former plays a more important role than the latter in controlling the relative positions of the two cage carbon atoms during the reductive process. If the number of bridging carbon atoms is three or four, CAd carborane anions are produced regardless of the rigidity of the bridges after reduction with group 1 metals. If the number of bridging carbon atoms is six, the cage carbon–carbon bond is completely broken during two-electron reduction to generate CAp *nido*-carborane dianions, regardless of the rigidity of the bridges. When the number of bridging carbon atoms is five, the rigidity of the bridge dominates the relative positions of the cage carbon atoms during the reduction process. A more rigid five-carbon-atom bridge locks the two cage carbon atoms on *ortho* positions, forming CAd carborane anions. On the other hand, a less rigid one allows the two cage carbon atoms to move apart, generating CAp *nido*-carborane dianions. This work also provides useful structural information for further studies on the preparation of supracarboranes.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen 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. 1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀ (**1**),⁹ 1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀ (**2**),¹⁰ 1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀ (**3**),⁹ and 1,2-(CH₂)₅-1,2-

C₂B₁₀H₁₀ (**4**)⁹ were prepared according to literature methods. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox, on a Perkin-Elmer 1600 Fourier transform spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 and 75.47 MHz, respectively. ¹¹B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts were reported in δ units with references to the residual protons 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 recorded on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by MEDAC Ltd., Middlesex, U.K.

Preparation of 1,2-(CH₂)₆-1,2-C₂B₁₀H₁₀ (5**).** To a solution of *o*-C₂B₁₀H₁₂ (3.60 g, 25.0 mmol) in a dry toluene/Et₂O (2:1, 50 mL) was added a 1.60 M solution of *n*-BuLi in *n*-hexane (31.3 mL, 50.0 mmol) dropwise with stirring at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was then cooled to 0 °C, and a solution of 1,6-dibromohexane (6.10 g, 25.0 mmol) in toluene/Et₂O (2:1, 30 mL) was slowly added with stirring. The reaction mixture was heated to reflux overnight and then quenched with 50 mL of water. After removal of the precipitate by filtration, the organic layer was separated, and the aqueous layer was extracted with Et₂O (50 mL \times 3). The combined organic portions were dried over anhydrous Na₂SO₄. After removal of the solvent, the resultant solid was subjected to silicon chromatographic separation (SiO₂, 300–400 mesh) using hexane as eluant to give **5** as a white powder (0.95 g, 17%). ¹H NMR (CDCl₃): δ 2.56 (t, *J* = 5.4 Hz, 4H, CH₂), 1.77 (m, 4H, CH₂), 1.64 (m, 4H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ 35.65, 26.16, 24.83 (CH₂), the cage carbons were not observed. ¹¹B{¹H} NMR (CDCl₃): δ -4.61 (2), -9.61 (4), -10.58 (2), -11.40 (2). IR (KBr, cm⁻¹): ν_{BH} 2584 (vs). HR-FABMS: *m/z* calcd for C₈H₂₂B₁₀, 226.2719; found, 226.2715.

Preparation of [1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅]₂ (6**).** To a THF (100 mL) solution of 1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀ (**1**; 5.52 g, 30.0 mmol) was added finely cut Li metal (1.80 g, 200 mmol), and the mixture was stirred at room temperature for 1 day, giving a red solution. Removal of excess Li and THF yielded a pale yellow solid. Recrystallization from THF afforded **6** as colorless crystals (14.6 g, 85%). ¹H NMR (pyridine-*d*₅): δ 3.64 (m, 20H, THF), 2.99 (m, 2H, CH₂CH₂CH₂), 2.84 (m, 2H, CH₂CH₂CH₂), 1.94 (m, 2H, CH₂CH₂CH₂), 1.62 (m, 20H, THF). ¹³C{¹H} NMR (pyridine-*d*₅): δ 67.19, 25.15 (THF), 45.05 (CH₂CH₂CH₂), 28.98 (CH₂CH₂CH₂), the cage carbons were not observed. ¹¹B{¹H} NMR (pyridine-*d*₅): δ 7.71 (2), 3.15 (2), -1.63 (3), -12.93 (1), -16.54 (1), -18.00 (1). IR (KBr, cm⁻¹): ν_{BH} 2510 (vs), 2427 (vs), 2355 (vs), 2280 (s). Anal. Calcd for C₂₁H₄₈B₁₀Li₄O₄ (**6** - THF): C, 50.40; H, 9.67. Found: C, 50.01; H, 9.86.

Preparation of [1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅]₂ (7**).** Following the procedure described for **6**, a solution of 1,2-(CH₂CH=CHCH₂)-1,2-C₂B₁₀H₁₀ (**2**; 0.39 g, 2.00 mmol) in THF (10 mL) was reacted with finely cut Li metal (0.09 g, 10.00 mmol) at room temperature. Recrystallization from THF afforded **7** as colorless crystals (0.96 g, 82%). ¹H NMR (pyridine-*d*₅): δ 6.93 (m, 1H, CH=CH), 5.80 (m, 1H, CH=CH), 3.64 (m, 20H, THF), 3.02 (m, 2H, CH₂), 2.88 (m, 2H, CH₂), 1.62 (m, 20H, THF). ¹³C{¹H} NMR (pyridine-*d*₅): δ 143.4, 139.2 (CH), 67.29, 25.22 (THF), 39.71 (CH₂), the cage carbons were not observed. ¹¹B{¹H} NMR (pyridine-*d*₅): δ 9.92 (2), 8.12 (2), -2.18 (3), -11.88 (1), -15.36 (1), -17.43 (1). IR (KBr, cm⁻¹): ν_{BH} 2512 (vs), 2348 (s). Anal. Calcd for C₂₆H₅₆B₁₀Li₄O₅ (**7**): C, 53.41; H, 9.66. Found: C, 53.79; H, 9.58.

Preparation of [1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀]{Li₄(THF)₅]₂ (8**).** Following the procedure described for **6**, a solution of 1,2-(CH₂)₄-1,2-C₂B₁₀H₁₀ (**3**; 0.40 g, 2.00 mmol) in THF (10 mL) was reacted with finely cut Li metal (0.09 g, 10.00 mmol) at room

Table 3. Crystal Data and Summary of Data Collection and Refinement for 6–10

	6	7	8	9	10
formula	C ₂₅ H ₅₄ B ₁₀ Li ₄ O ₅	C ₂₆ H ₅₆ B ₁₀ Li ₄ O ₅	C ₂₆ H ₅₈ B ₁₀ Li ₄ O ₅	C ₂₃ H ₅₂ B ₁₀ Na ₂ O ₄	C ₂₄ H ₅₄ B ₁₀ Na ₂ O ₄
cryst size (mm)	0.60 × 0.50 × 0.30	0.50 × 0.40 × 0.20	0.60 × 0.50 × 0.40	0.50 × 0.40 × 0.20	0.40 × 0.10 × 0.10
fw	572.6	584.6	586.6	546.7	560.8
cryst syst	triclinic	triclinic	triclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> , Å	10.788(1)	12.195(1)	10.952(1)	16.930(3)	18.991(4)
<i>b</i> , Å	13.079(1)	12.277(1)	13.087(1)	11.470(2)	15.089(3)
<i>c</i> , Å	14.710(2)	13.921(1)	14.999(1)	33.827(7)	12.380(3)
α , deg	114.82(1)	71.87(1)	115.80(1)	90	90
β , deg	102.68(1)	67.17(1)	103.91(1)	90	93.09(3)
γ , deg	97.49(1)	84.61(1)	95.79(1)	90	90
<i>V</i> , Å ³	1778.8(4)	1824.6(2)	1826.0(2)	6569(2)	3542.4(13)
<i>Z</i>	2	2	2	8	4
<i>D</i> _{calcd} , Mg/m ³	1.069	1.064	1.067	1.106	1.051
radiation (λ), Å	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ range, deg	3.2 to 50.0	3.5 to 48.0	3.2 to 48.0	4.4 to 48.0	4.3 to 48.0
μ , mm ⁻¹	0.063	0.063	0.063	0.088	0.083
<i>F</i> (000)	616	628	632	2352	1208
no. of obsd reflns	4633	4762	4764	3351	2124
no. of params refined	437	446	446	352	210
goodness of fit	1.103	1.081	1.067	1.188	2.608
R1	0.081	0.096	0.078	0.098	0.084
wR2	0.235	0.277	0.219	0.249	0.267

temperature. Recrystallization from THF afforded **8** as colorless crystals (1.00 g, 85%). ¹H NMR (pyridine-*d*₅): δ 3.68 (m, 20H, THF), 2.92 (m, 4H, CH₂CH₂CH₂CH₂), 1.65 (m, 24H, THF + CH₂CH₂CH₂CH₂). ¹³C{¹H} NMR (pyridine-*d*₅): δ 65.26, 23.21 (THF), 33.35 (CH₂CH₂CH₂CH₂), 20.06 (CH₂CH₂CH₂CH₂), the cage carbons were not observed. ¹¹B{¹H} NMR (pyridine-*d*₅): δ 9.64 (4), -1.07 (2), -10.62 (1), -16.34 (3). IR (KBr, cm⁻¹): ν_{BH} 2499 (vs), 2421 (vs), 2353 (vs), 2280(s). Anal. Calcd for C₂₆H₅₈B₁₀Li₄O₅ (**8**): C, 53.24; H, 9.97. Found: C, 52.74; H, 9.99.

Preparation of [{1,3-(CH₂)₅-1,3-C₂B₁₀H₁₀ } {Na₂(THF)₄ }]_n (**9**). To a THF (25 mL) solution of 1,2-(CH₂)₅-1,2-C₂B₁₀H₁₀ (**4**; 0.21 g, 1.00 mmol) was added finely cut Na metal (0.21 g, 9.13 mmol), and the mixture was stirred at room temperature for a week. After removal of excess Na, the clear pale yellow solution was concentrated to about 10 mL, to which was added toluene (~10 mL). Complex **9** was isolated as colorless crystals after this solution stood at room temperature for 2 days (0.42 g, 77%). ¹H NMR (pyridine-*d*₅): δ 3.64 (m, 16H, THF), 2.97 (m, 4H, CH₂), 2.71 (m, 4H, CH₂), 2.67 (m, 2H, CH₂), 1.60 (m, 16H, THF). ¹³C{¹H} NMR (pyridine-*d*₅): δ 67.16, 25.13 (THF), 40.04, 35.69, 25.78 (CH₂); the cage carbon atoms were not observed. ¹¹B{¹H} NMR (pyridine-*d*₅): δ -0.07 (2), -13.37 (2), -16.47 (4), -26.36 (2). IR (KBr, cm⁻¹): ν_{BH} 2580 (vs), 2460 (s). Anal. Calcd for C₂₁H₄₈B₁₀Na₂O_{3.5} (**9** - 0.5 THF): C, 49.39; H, 9.47. Found: C, 48.98; H, 9.35.

Alternative Method. To a THF (25 mL) solution of 1,2-(CH₂)₅-1,2-C₂B₁₀H₁₀ (**4**; 0.21 g, 1.00 mmol) was added finely cut lithium metal (0.09 g, 10.0 mmol), and the mixture was stirred at room temperature for a week. Removal of excess Li metal and THF afforded a pale yellow sticky solid, presumably *nido*-[(CH₂)₅C₂B₁₀H₁₀][Li₂(THF)_x]. Cation exchange with NaI (0.60 g, 4.00 mmol) in THF (5 mL) gave **9** as colorless crystals (0.38 g, 70%).

Preparation of [{1,4-(CH₂)₆-1,4-C₂B₁₀H₁₀ } {Na₂(THF)₄ }]_n (**10**). This complex was prepared as colorless crystals using the same procedure described for **9** from 1,2-(CH₂)₆-1,2-C₂B₁₀H₁₀ (**5**; 0.23 g, 1.00 mmol) and finely cut Na metal (0.23 g, 10.0 mmol) in THF (25 mL): yield 0.45 g (80%). ¹H NMR (pyridine-*d*₅): δ 3.64 (m, 16H, THF), 3.14 (m, 4H, 2.97, CH₂), 2.52 (m, 8H, CH₂), 1.60 (m, 16H, THF). ¹³C{¹H} NMR (pyridine-*d*₅): δ 67.16, 25.13 (THF), 39.31, 30.24, 29.02 (CH₂); the cage carbon atoms were not observed. ¹¹B{¹H} NMR (pyridine-*d*₅): δ 15.00 (2B), -8.81 (2B), -16.52 (4B), -22.70 (2B). IR (KBr, cm⁻¹): ν_{BH} 2583 (vs), 2340 (w). Anal. Calcd for C₂₁H₅₀B₁₀Na₂O_{3.5} (**10** - 0.5THF): C, 50.36; H, 9.60. Found: C, 50.39; H, 9.37.

Alternative Method. To a THF (25 mL) solution of 1,2-(CH₂)₆-1,2-C₂B₁₀H₁₀ (**5**; 0.23 g, 1.00 mmol) was added finely cut lithium metal (0.09 g, 10.0 mmol), and the mixture was stirred at room temperature for a week. Removal of excess Li metal and THF afforded a pale yellow sticky solid, presumably *nido*-[(CH₂)₆C₂B₁₀H₁₀][Li₂(THF)_x]. Cation exchange with NaI (0.60 g, 4.00 mmol) in THF (5 mL) gave **10** as colorless crystals (0.41 g, 73%).

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N₂ in thin-walled glass capillaries. 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.¹² 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.¹³ The bridging methylene unit in **10** was disordered over two positions with 0.54:0.46 occupancies. All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 3.

Acknowledgment. The work described in this paper was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK 4026/02P) and Direct Grant (2060274).

Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **6**–**10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050683X

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