Carboracycles: Macrocyclic Compounds Composed of Carborane Icosahedra Linked by Organic Bridging Groups

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A family of macrocyclic compounds are described, together with their precursors. These cycles are composed of icosahedral carboranes linked *via* their carbon vertices through 1,3-trimethylene, α,α′-1,3-xylylene, or α,α′-2,6-lutidylene groups. The compounds *cyclo*-(1,3-trimethylene-1′,2′-*closo*-1′,2′-$C_2B_{10}H_{10})_4$ (**6a**), *cyclo*-(1,3-trimethylene-1′,2′-*closo*-9′,12′-dimethyl-1′,2′-$C_2B_{10}H_8)_4$ (**6b**), *cyclo*-(1,3-trimethylene-1′,2′-*closo*-1′,2′-$C_2B_{10}H_{10})_3$ (**9**), *cyclo*-(α,α′-1,3-xylylene-1′,2′-*closo*-1′,2′-$C_2B_{10}H_{10})_2$ (**11a**), *cyclo*-(α,α′-1,3-xylylene-1′,7′-*closo*-1′,7′-$C_2B_{10}H_{10})_2$ (**11b**), *cyclo*-(α,α′-1,3-xylylene-1′,7′-*closo*-9′,10′-dimethyl-1,7-$C_2B_{10}H_8)_2$ (**11c**), *cyclo*-(α,α′-1,3-xylylene-1′,2′-*closo*-1′,2′-$C_2B_{10}H_{10})_4$ (**12**), *cyclo*-(α,α′-1,3-xylylene-1′,7′-*closo*-1′,7′-$C_2B_{10}H_{10})_3$ (**13**), *cyclo*-(α,α′-2,6-lutidylene-1′,7′-*closo*-1′,7′-$C_2B_{10}H_{10})_2$ (**19**), and *cyclo*-(α,α′-2,6-lutidylene *N*-oxide−1′,7′-*closo*-1′,7′-$C_2B_{10}H_{10})_2$ (**20**) have been synthesized. The structures of **6a**, **6b**, **9**, **11a**, **11b**, **11c**, **12**, and **19** have been determined by X-ray crystallography. Crystal data: for **6a**, triclinic, space group $P\bar{1}$, $a = 11.131(2)$ Å, $b = 12.642(2)$ Å, $c = 12.996(2)$ Å, $\alpha = 84.383(6)°$, $\beta = 65.884(6)°$, $\gamma = 97.292(5)°$, $Z = 1$, $R = 0.079$; for **6b**, monoclinic, space group $P2_1/a$, $a = 13.500(2)$ Å, $b = 31.141(3)$ Å, $c = 13.831(2)$ Å, $\beta = 99.90(1)°$, $Z = 2$, $R = 0.097$; for **11a**, monoclinic, space group $C2/c$, $a = 14.5682(8)$ Å, $b = 14.5046(8)$ Å, $c = 16.1998(8)$ Å, $\beta = 95.631(2)°$, $Z = 4$, $R = 0.081$; for **11b**, monoclinic, space group $P2_1/n$, $a = 11.650(2)$ Å, $b = 10.606(2)$ Å, $c = 11.730(2)$ Å, $\beta = 104.951(6)°$, $Z = 2$, $R = 0.069$; for **11c**, orthorhombic, space group *Pbca*, $a = 12.532(2)$ Å, $b = 14.271(2)$ Å, $c = 18.143(3)$ Å, $Z = 4$, $R = 0.076$; for **19**, orthorhombic, space group *Pcab* (No. 61, standard setting *Pbca*), $a = 11.0428(6)$ Å, $b = 11.3785(6)$ Å, $c = 22.533(1)$ Å, $Z = 4$, $R = 0.074$.

Introduction

The development of synthesis routes aimed at the production of nanometer-scale, structurally well-defined and rigid molecules has become a rapidly expanding frontier in chemistry.[1] Entities of this type bridge the gap between discrete molecules and bulk materials, having a degree of structural precision in their internal composition which allows control of their chemical properties, but a size which is hopefully commensurate with the smallest structures available from current micromanufacturing techniques. One "bottom-up" approach to well-ordered materials requires first the design of individual components, or modules, and then their assembly into larger ordered structures. In a convergent approach to these assemblies, there may be a hierarchy of modules, each "generation" made up by assembling members of the next smaller generation.

At the lowest modular level, we are investigating the potential of the three icosahedral carborane isomers,[2] commonly known as *o*-, *m*-, and *p*-carborane (or 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$, respectively) as subunits for the assembly of larger arrays. The carboranes have several desirable features in this regard. Their rigid three-dimensional structure is exactly what is required to hold substituents in well-defined spatial relationships. While many transition elements exert similar control over the stereochemistry of their ligands, carboranes have an additional advantage in being superior in both thermal and chemical stability to most organic and organometallic compounds. Regardless of the carborane isomer, the two carbon vertices bear relatively acidic protons and readily allow substitution with metals or organic groups,[2] and substituents can also be introduced with at least a certain few of the boron vertices with good control.[2c] In addition, it is possible to replace boron vertices with transition elements, with the carborane moiety isolobal to the cyclopentadienyl group in metallocenes.[2d] It therefore seems reasonable that suitably derivatized carboranes can act as a family of building blocks to be connected in a variety of ways while maintaining good control over the physical shape of the product. In publications by us and others several classes of compounds have been described using this approach. These include linear rigid rod molecules made up by direct coupling of the carbon vertices of *p*-carborane,[3] hybrid linear rods made by joining opposite boron vertices of *p*-carborane icosahedra through acetylene or diacetylene linkers,[4] nonlinear oligomers of both *o*- and *m*-carborane,[5] cycles of *o*-carborane icosahedra connected *via* their carbon vertices through mercury atoms,[6] and cycles of *m*-carborane icosahedra joined *via* boron vertices with mercury atom linkers.[7]

We here describe the synthesis of macrocyclic compounds composed of *o*- and *m*-carboranes joined through their carbon

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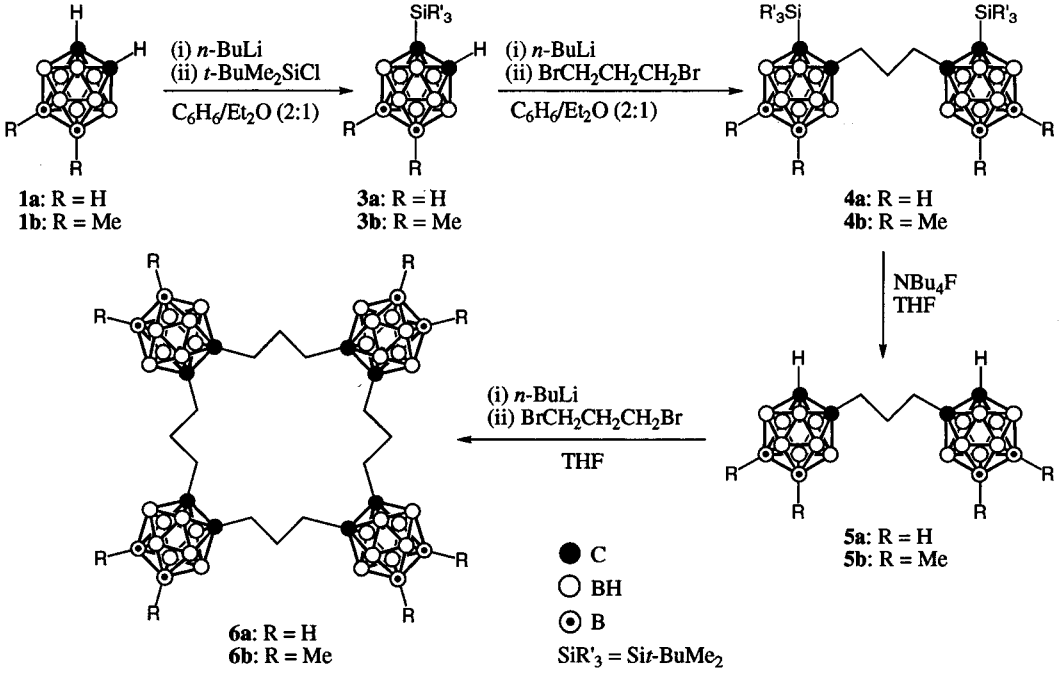
Scheme 1



vertices by a series of bifunctional organic linking groups of varying complexity. Attempts to synthesize cycles composed purely of either *o*- or *m*-carborane units have so far been unsuccessful, presumably due either to the insolubility of the required intermediates or to unacceptable angle strain in transition states leading to closure of the cycles. However, by including bifunctional linker groups to connect carbon vertices of adjacent icosahedra, a wide variety of cyclic compounds become accessible, having a range of cavity sizes and varying degrees of flexibility. There are rather few examples in the literature of cyclic compounds containing multiple carborane units.[8] This is partially due to the lack, until recently, of a suitable protecting group for one of the two carbon vertices of *o*-carborane, the most readily available isomer. In the absence of a protective group which renders *o*-carborane temporarily monofunctional at carbon, bifunctional electrophiles tend to form exocyclic derivatives with bridges connecting both carbon vertices of a single carborane.[9] We have found the *tert*-butyldimethylsilyl group to be an excellent protecting group for a carbon vertex of *o*-carborane.[10] Recent studies indicate that metalation in dimethoxyethane allows substitution at a single carbon vertex in a controlled fashion.[11] It is also possible to protect one carbon vertex of *m*-carborane with a silyl group, although due to the relative positions of the carbon vertices, exocyclic derivatives are less likely to form in the absence of such a group. Using these methods, we here report the syntheses of a family of "carboracycles" of different sizes, including either *o*- or *m*-carboranes linked by bifunctional organic spacers.[12]

Results and Discussion

The simplest form of carboracycle is one in which the carborane subunits are joined by an alkylene linker. Scheme 1 shows the rational synthesis of a trimethylene-linked tetramer starting from *o*-carborane (**1a**). *o*-Carborane has two acidic CH vertices which can be deprotonated with *n*-butyllithium to provide a dilithio derivative which reacts readily with electrophiles. The use of an alkyl halide as electrophile provides a convenient synthetic method for the alkylation of carbon vertices. Reaction of **1a** with 1 molar equiv of *n*-butyllithium, followed by addition of *tert*-butyldimethylsilyl chloride yielded 1-(*tert*-butyldimethylsilyl)-*o*-carborane (**3a**) in essentially quantative yield. Further reaction of **3a** with *n*-butyllithium and addition of $^1/_2$ molar equiv of the bifunctional electrophile 1,3-dibromopropane afforded dimer **4a** in 54% yield, in which two carboranes are linked by a trimethylene bridge. Compound **4a** was easily and quantitatively desilylated with fluoride ion to give the unprotected dimer **5a**. Compounds **3a**,[10] **4a**[10b] and **5a**[10b] have been previously described. Deprotonation of the resulting CH vertices of **5a**, followed by reaction with a further 1 molar equiv of 1,3-dibromopropane yielded the cyclic tetramer **6a** in 87% yield. Compound **6a** was found to be essentially insoluble in common organic solvents, and this impeded its characterization. A ^{1}H NMR spectrum taken in dimethylacetamide-d_9 contains no carborane CH signal, which is consistent with cyclization, but the ^{11}B{^{1}H} NMR is uninformative, displaying only two broad peaks in a 1:4 ratio. The compound is too insoluble to obtain ^{13}C NMR data. However, the EI mass spectrum conclusively demonstrates the formation of a cyclic

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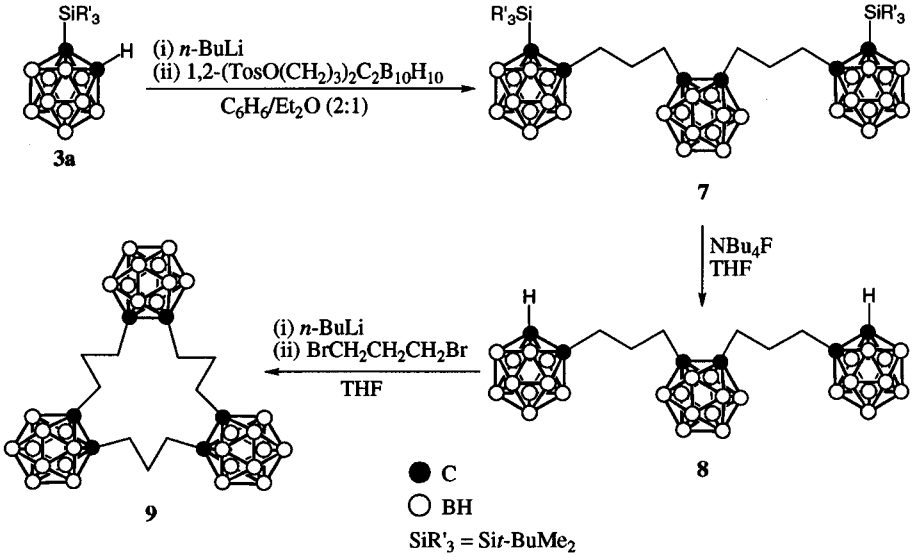
Scheme 2



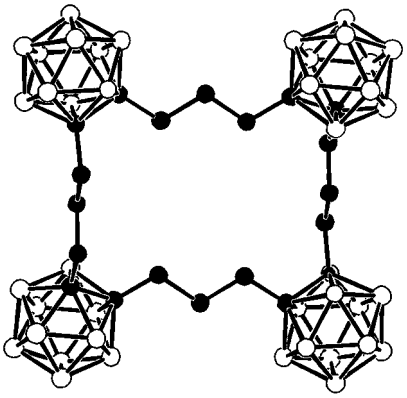


Figure 1. ORTEP representation of compound **6a**, excluding hydrogen atoms.[23]

tetramer, and a crystal suitable for an X-ray diffraction study was grown from hot dimethylacetamide solution. The structure is pictured in Figure 1. The cages in compound **6a** share a common plane, with two opposing trimethylene linkers also being in plane while the other two linkers lie above and below the plane of the molecule, respectively.

The cyclization reaction to form **6a** by a bifunctional nucleophilic displacement mechanism is remarkably efficient, considering that two molecules of **5a** and two molecules of 1,3-dibromopropane must be induced to come together with no apparent template to drive the reaction. However, no cyclic dimer was observed in the product mixture by mass spectrometry. Formation of the dimer is presumably disfavored due to angle strain associated with closure of the cycle using such a short linking group, since entropic considerations would seem to favor assembly of the dimer. There was also no evidence suggesting the formation of oligomeric material.

Limited solubility associated with arrays containing multiple carborane units is a common problem, which we have previously addressed in the synthesis of "mercuracarborands"[6a,13] by the use of 9,12-dimethyl-*o*-carborane (**1b**),[14] a derivative of **1a** bearing methyl groups on the two boron vertices furthest removed from the carbon vertices of the cage. A set of reactions parallel to those described above starting with compound **1b**

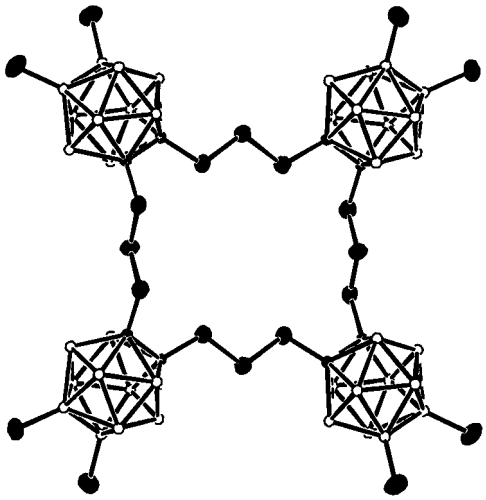


Figure 2. ORTEP representation of compound **6b**, excluding hydrogen atoms.[23]

yielded the cyclic tetramer **6b**, which dissolves well in THF and to a limited extent in dichloromethane and chloroform. The structure of compound **6b** was also determined by X-ray crystallography and is shown in Figure 2. Compound **6b** is in most respects similar to **6a**, although it was possible to obtain more satisfactory spectral data including a $^{13}C\{^1H\}$ NMR spectrum. The methyl groups attached to the boron vertices appear at 0.15−0.20 ppm in the ^1H NMR spectrum, and provide a useful NMR signal to monitor the degree of purity of **6b**, since only upon cyclization do the two methyl groups on each carborane cage become equivalent.

A method similar to that used for the synthesis of compounds **6a** and **6b** was used to create a trimethylene-linked cyclic trimer (Scheme 2). Lithiation of **3a** was followed by reaction with a ditosyl derivative of *o*-carborane to yield the trimeric trimethylene-linked precursor **7**, which was desilylated with fluoride ion to yield compound **8**.[15] Deprotonation of compound **8** with *n*-butyllithium followed by treatment with 1 molar equiv of 1,3-dibromopropane afforded the cyclic trimer **9**. Compound **9** shows similar spectral characteristics to **6a**, and both mass spectrometry and X-ray crystallography (Figure 3) unequivocally demonstrate its identity.[12] In the crystal, the trimethylene linkers

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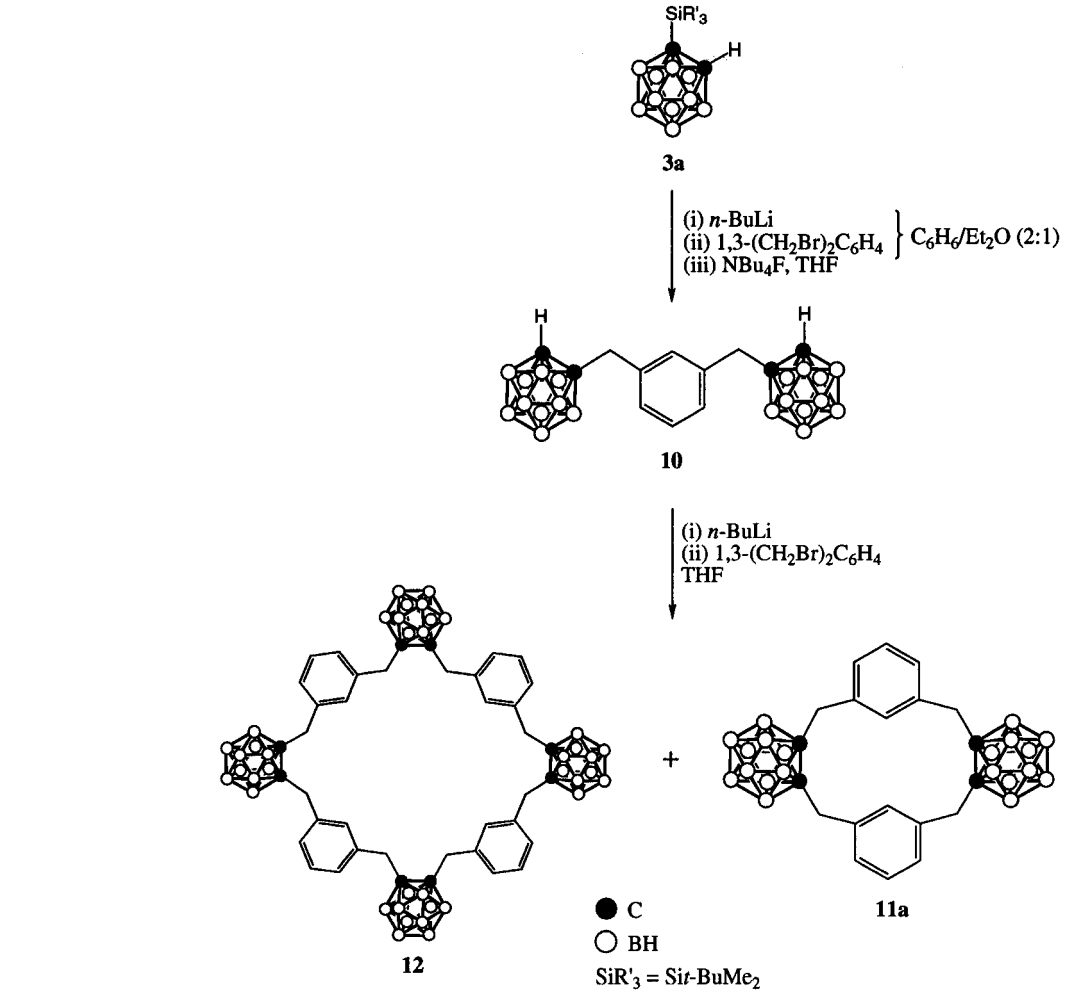
Scheme 3



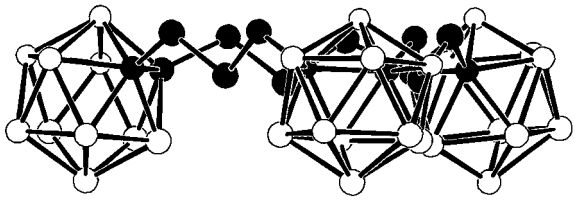


Figure 3. ORTEP representation of compound **9**, excluding hydrogen atoms.[23]

constrain all three carborane icosahedra to tilt out of the plane of the cycle in the same direction, giving the molecule a definite "top" and "bottom". However, the NMR data suggest that the molecule is fairly flexible and has a low barrier to inversion, since no especially broad peaks appear in any of the spectra. Unlike the cyclizations leading to compounds **6a** and **6b**, two molecules of **8** did not react with two molecules of 1,3-dibromopropane to form a cyclic hexamer; the trimer was the only cyclic product observed.

Also investigated was the formation of carboracycles using a linker which incorporated an aromatic group. Using the modular synthesis strategy described above, the lithio salt of **3a** was treated with α,α'-dibromo-1,3-xylene ($^1/_2$ molar equiv) and then deprotected with fluoride ion to yield the dimer **10**.[6b] Further deprotonation and reaction with the same bifunctional electrophile afforded a mixture of both dimeric and tetrameric cyclic products **11a** and **12**, respectively, in *ca.* 1:2 ratio (Scheme 3), together with some unidentified and presumably oligomeric viscous material. Separation of **11a** and **12** proved to be difficult, but a small quantity of each product was isolated

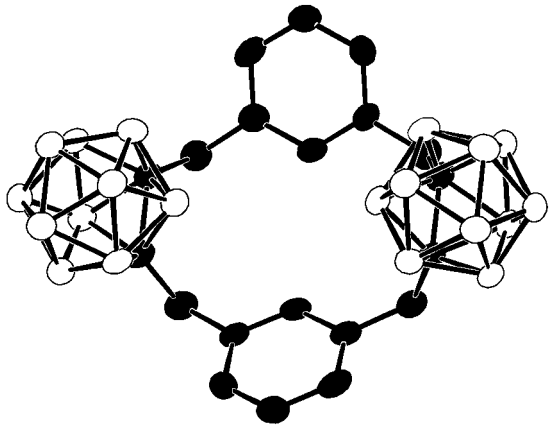
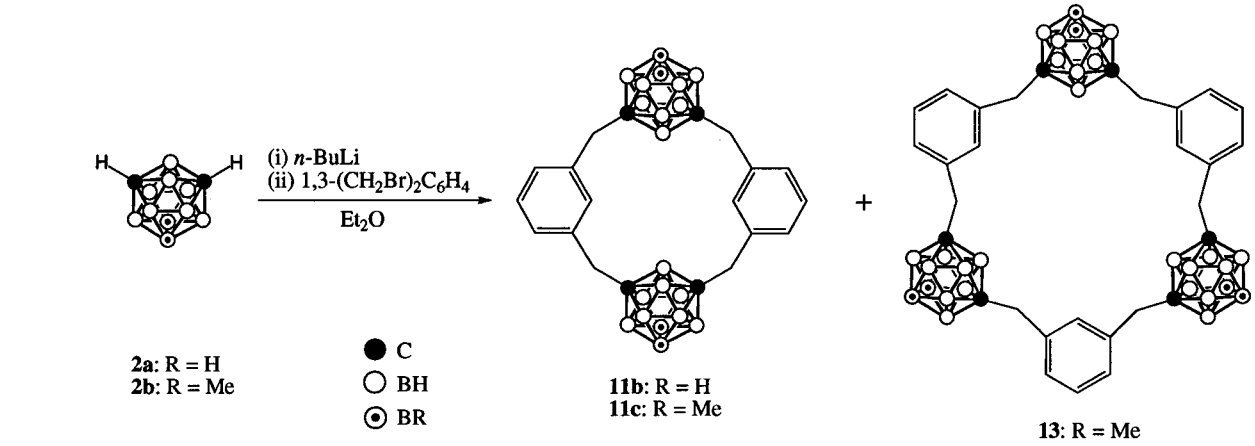


Figure 4. ORTEP representation of compound **11a**, excluding hydrogen atoms.[23]

in pure form by fractional crystallization. Slow evaporation of a THF solution of the product mixture allowed the isolation of **12** in 38% yield, and recrystallization of the remaining material from ethyl acetate afforded **11a** in 9% yield. Both products were characterized spectroscopically and by X-ray crystallography; the structure of **11a** is shown in Figure 4 and that of **12**[12] is shown in Figure 5. Compound **11a** adopts a bowl-shaped conformation in the crystal with the planes defined by the atoms of the phenyl rings meeting at an angle of approximately 80°. In Figure 4 the molecule is viewed looking into the "bowl". In compound **12**, the phenyl rings are coplanar, with one adjacent pair of carboranes above the plane and the other pair below the

Scheme 4



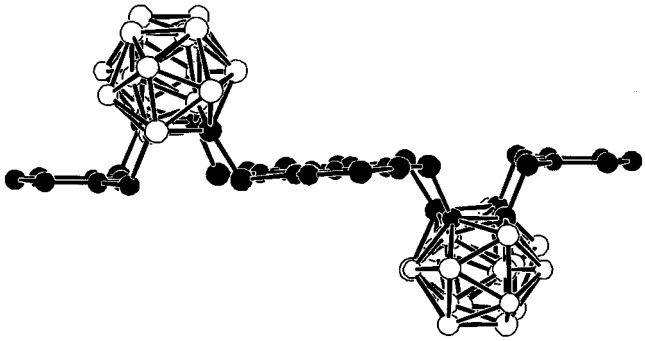


Figure 5. ORTEP representation of compound **12**, excluding hydrogen atoms.[23]

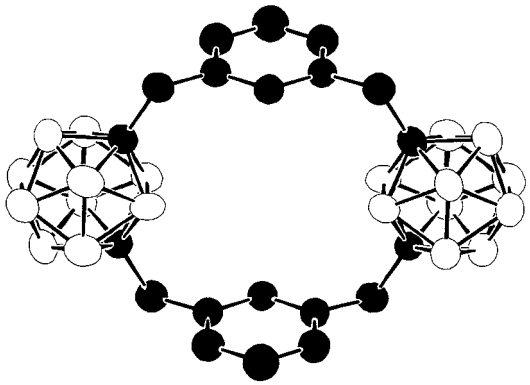


Figure 6. ORTEP representation of compound **11b**, excluding hydrogen atoms.[23]

plane. The position of the resonance of the hydrogen attached to the 2-position of the 1,3-xylylene group in the ^{1}H NMR spectrum provides a quick method to distinguish between the two compounds during the separation procedure; in **11a** this singlet resonance is present at 7.84 ppm in deuteroacetone, whereas in **12** the resonance appears at 7.35 ppm in the same solvent. Both compounds were found to be relatively insoluble in organic solvents, especially **12**, for which a ^{13}C NMR spectrum was not obtainable.

While the chemistries associated with the carbon vertices of the *ortho*- and *meta*-icosahedra are similar, the differences in geometry create some differences in synthetic methodology. The strategy described above for constructing *o*-carborane-containing carboracycles is based upon a stepwise protection and deprotection protocol in which the *tert*-butyldimethylsilylated *o*-carborane module acts as the primary synthon. The sizes and conformations of the resulting carboracycle arrays are sensitive to the choice of the organic linkage. Similarly, incorporation of *m*-carborane subunits into carboracycles allows for a degree of variation of the angle strain associated with cyclization of these species. However, the wider separation between the carbon vertices of the *m*-carborane cage makes exocyclic ring formation from a single bifunctional cage and a bifunctional electrophile possible only if the electrophile is very long and flexible. Therefore, we have found that the *tert*-butyldimethylsilyl protecting group is unnecessary for the preparation of a number of *m*-carborane-based carboracycles.

Lithiation of *m*-carborane (**2a**) with 2 molar equiv of *n*-butyllithium produced the dilithiated *m*-carborane *in situ*. Treatment of this reagent with α,α′-dibromo-1,3-xylene in a 1:1 ratio afforded the cyclic dimer **11b** in 71% yield (Scheme 4). The X-ray diffraction structure of **11b** is shown in Figure 6. Unlike **11a**, in **11b** the phenyl rings lie parallel to one another. However, they are offset and there is no evidence of π-stacking in the molecule or the extended structure of the crystal. The improvements in yield and simplicity of the reaction, when compared to the *o*-carborane system, make this an attractive route to carboracycle products, and it is interesting to note that only the dimeric product is formed with no larger cycles being observed. The formation of a single cycle was initially attributed to the formation of the least strained product. However, since **11b** showed rather limited solubility in organic solvents, the same reaction was carried out using 9,10-dimethyl-*m*-carborane[14] (**2b**) rather than **2a** (Scheme 4). While this reaction also gave a high yield of cyclic products (82 % total), two carboracycles were found in the product mixture in *ca*. 4:1 ratio: the dimeric cycle **11c** and the trimeric cycle **13**. Both compounds were markedly more soluble in organic solvents than **11b**. This result suggests that the solubility of intermediate species plays an important role in determining the ultimate ring size of a carboracycle in the ring formation process. The same reaction was carried out in high dilution with slow addition of α,α′-dibromo-1,3-xylene controlled by an automatic syringe. Under these conditions, the product distribution of **11c** and **13** appeared to remain essentially the same as before, although this could only be monitored by mass spectrometry of the product mixture as there are no useful NMR markers to differentiate the two compounds. The structure of **11c** was determined by X-ray diffraction and is shown in Figure 7, but high quality single crystals of **13** were not obtained. Compound **11c** shows no significant structural differences from **11b**.

Having established that it is possible to synthesize cyclic products having a variety of sizes and geometries and to produce cycles with acceptable solubilities for performing further chemistry, our attention has now turned to methods of synthesizing functionalized carboracycles. With suitable functionalization, such species might interact with transition metal ions

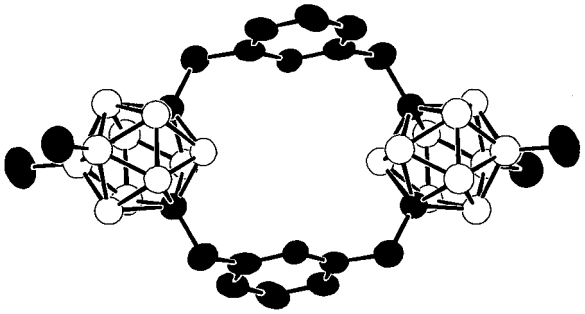


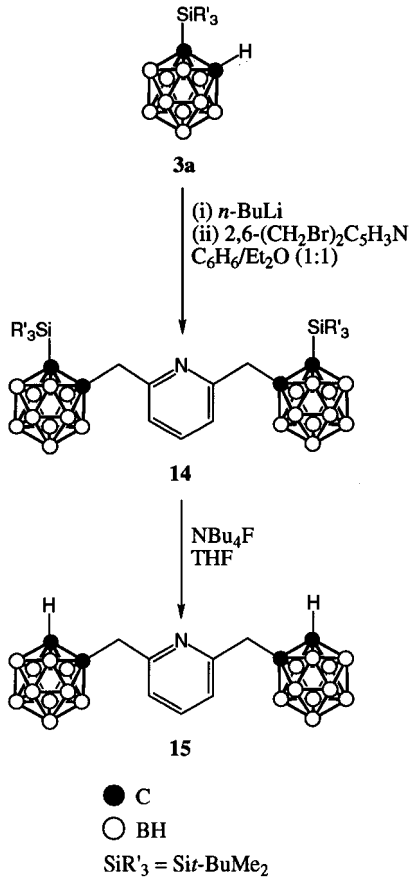
Figure 7. ORTEP representation of compound **11c**, excluding hydrogen atoms.[23]

as complex ligands or even be used as the basis of a *rotaxane* or *catenane* chemistry. The potential for introducing functional groups into the cycle by the correct choice of electrophile is considerable. A preliminary investigation of the scope of this methodology was concentrated upon the 2,6-lutidyl group. The aromatic nitrogen functionality present in this structure would be directed into the center of a cycle in which it was incorporated. Reaction of **3a** with *n*-butyllithium followed with $^1/_2$ molar equiv of α,α′-dibromo-2,6-lutidine[16] afforded the α,α′-2,6-lutidylene-linked silylated dimer **14**, which was desilylated with fluoride ion to yield the carboracycle precursor **15** (Scheme 5). Unexpectedly, however, lithiation of **15** and further reaction with α,α′-dibromo-2,6-lutidine did not result in the formation of any detectable cyclic product, merely the retrieval of starting materials.

On the basis of the superior ability of *m*-carborane subunits to support cyclization with α,α′-1,3-xylylene linkers, reaction of the dilithio salt of **2a** with α,α′-dibromo-2,6-lutidine was next investigated (Scheme 6). Using a simple synthetic protocol similar to that shown in Scheme 4 again did not lead to the expected cyclic products. Instead, compound **16**, comprising a single *m*-carborane attached to one "arm" of the lutidyl group, was isolated in 55% yield. However, the remaining bromomethyl group in **16** could be further reacted with 1 molar equiv of *mono*-lithiated *m*-carborane to yield **17** in 62% yield. Compound **17** was also directly accessible by reaction of α,α′-dibromo-2,6-lutidine with 2 molar equiv of monolithiated *m*-carborane in 53% yield. Alternatively, lithiation of *m*-carborane with 2 molar equiv of *n*-butyllithium followed by reaction with 2 molar equiv of α,α′-dibromo-2,6-lutidine afforded compound **18** in 41% yield. Species **18** was comprised of a *m*-carboranyl group with both carbon vertices linked to α-bromolutidyl moieties. The desired α,α′-2,6-lutidylene-bridged *m*-carborane cyclic dimer **19** was prepared from both **17** and **18**, either by reaction with *n*-butyllithium followed by α,α′-dibromo-2,6-lutidine or by reaction with the dilithio derivative of *m*-carborane, respectively. The X-ray structure of **19** is shown in Figure 8, and it is similar to the structures of **11b** and **11c** with the planes of the pyridyl rings lying parallel and offset. One consequence of this arrangement is that it would not be possible for both nitrogen atoms to simultaneously coordinate to a single substrate without significant distortion of the structure.

Attempts to quaternize the nitrogen centers of the lutidyl groups of **19** with methylating agents such as trimethyloxonium tetrafluoroborate and methyl triflate were not successful. This inert character of the nitrogen atoms may well be due to the electron-withdrawing effect of the carborane cages, which has been well-documented,[17] combined with stereochemical effects. However, treatment of **19** with 2 equiv of 3-chloroperoxybenzoic acid in methylene chloride at room temperature resulted in the isolation of the bis(*N*-oxide) carboracyclic derivative **20** in 79% yield (Scheme 7).

Scheme 5



A second route to functionalized carboracycles is by degradation of the *closo*-carborane subunits to the corresponding *nido*-structures. Reaction of *o*-carborane with strong base, such as a concentrated solution of ethanolic potassium hydroxide, affords a monoanionic *nido*-carborane $[C_2B_9H_{12}]^-$ in which one of the two boron vertices adjacent to the two carbon vertices has been excised, leaving an open pentagonal face in which two borons are bridged by an *endo*-hydrogen atom.[18] Removal of this hydrogen atom as a proton with sodium hydride affords the dianionic "dicarbollide" ion,[19] in which the pentagonal face is isolobal with a cyclopentadienyl group. A rich chemistry is associated with the dicarbollide ion, with the vacant vertex either being "reconstructed" with a boron atom carrying a substituent[20] or coordinated to a wide variety of transition metal[2d] or main group[21] ions. Our preliminary investigations show that it is possible to degrade the icosahedra of the *o*-carborane carboracycles, but not the *m*-carborane carboracycles. As a rule, *m*-carborane cages are more difficult to degrade than *o*-carboranes, and cages which are substituted on the carbon

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(17) (a) Hawthorne, M. F.; Berry, T. E.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 4746. (b) Alder, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 6174.

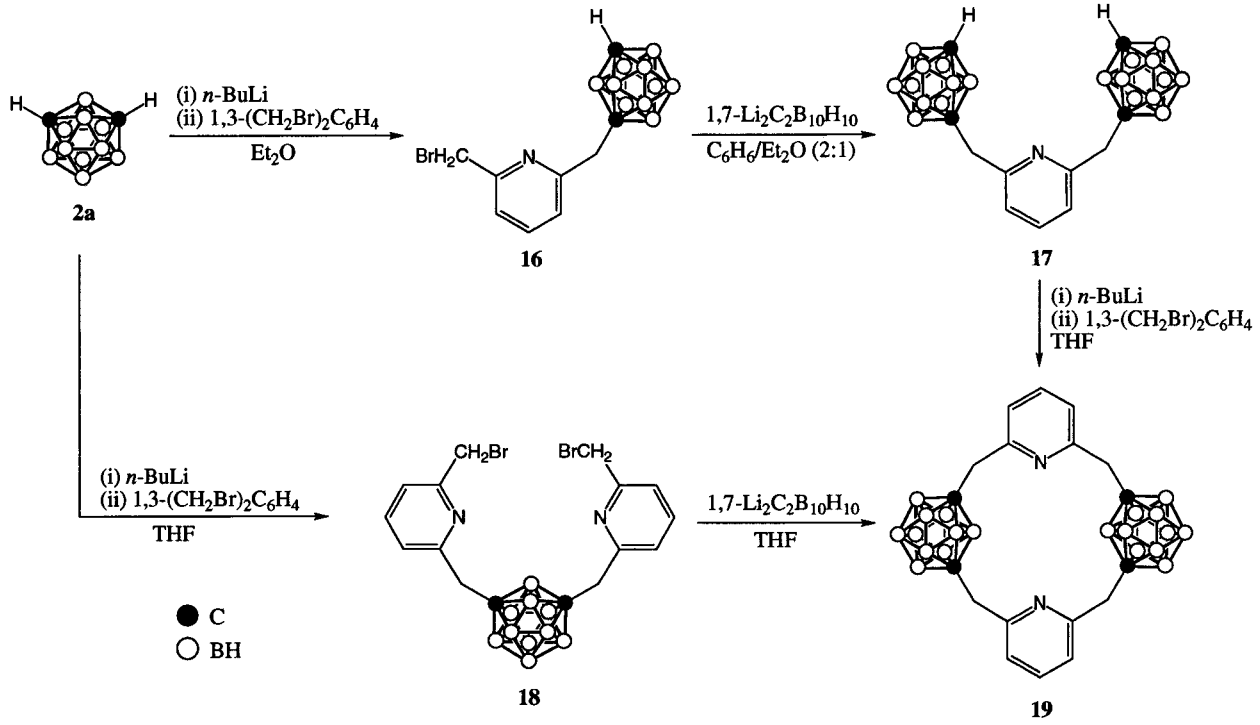
(18) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(19) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.

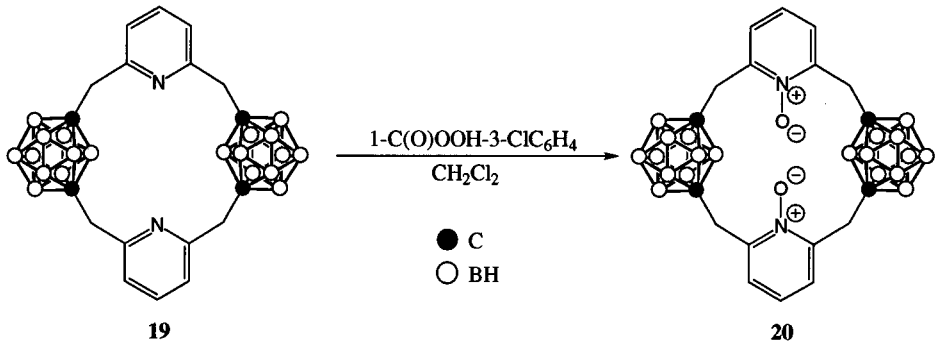
(20) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 896.

(21) (a) Popp, G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 6553. (b) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Churchill, M. R.; Reis, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 6663. (c) Schubert, D. M.; Rees, W. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2938.

Scheme 6



Scheme 7



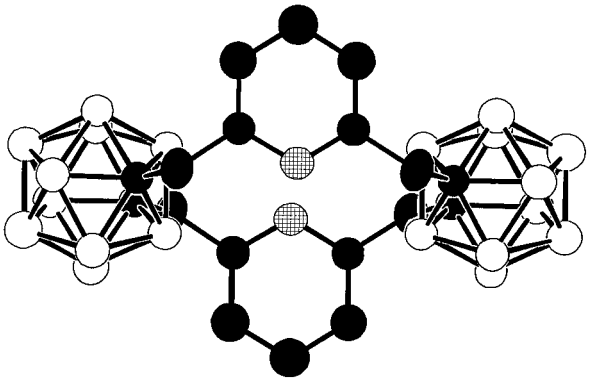


Figure 8. ORTEP representation of compound **19**, excluding hydrogen atoms. Nitrogen atoms are represented as hatched spheres.[23]

vertices are similarly more difficult to degrade than unsubstituted cages. The formation of a ring system which affords steric protection to the most electrophilic boron vertices (the 3- and 6-positions, located between the carbon vertices) appears to completely shut off this reaction pathway. In degradation reactions with the *o*-carborane-based cycles, there appears to be no control over which of the susceptible boron vertices on each cage (either the 3- or 6-position) is removed. Consequently, reaction products are typically a mixture of isomers which are not easily separated by conventional means. It seems likely, however, that these isomers will function as excellent multivalent ligands with different properties dictated by their specific geometries, and there appears to be a wide variety of reactions which these *nido*-cycles may undergo with cationic species.

Conclusions

We have described a family of macrocyclic compounds composed of alternating carborane icosahedra and organic linking groups. These compounds can be prepared in good yields by rational synthetic procedures. The size and geometry of the cycles, the identity of the carborane fragments, and the nature of the linking groups can all be varied in a controlled fashion to give a variety of novel structures. There appears to be good potential to include reactive centers into the cycles, either as linker group substituents or by modification of the carborane icosahedra, thus opening the way to large multivalent species capable of interaction with either transition metal centers or other electrophilic guests.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of argon using standard Schlenk techniques. All solvents used were reagent grade. Dichloromethane was distilled from calcium

hydride. THF and diethyl ether were distilled over sodium benzophenone ketyl. Benzene and toluene were distilled over sodium metal. α,α′-Dibromo-*m*-xylene was purchased from Aldrich Chemical Co. and used as received. *n*-Butyllithium was purchased from Aldrich and used without further treatment other than occasional titration to verify concentration.[22] Deuterated solvents were purchased from Cambridge Isotope Laboratories. α,α′-Dibromo-2,6-lutidine was prepared by a published procedure.[16] *o*-Carborane and *m*-carborane were purchased from Consumer Health Research of Los Angeles. ^{1}H NMR spectra were recorded using a Bruker AM-200 spectrometer at 200 MHz, ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer at 90.9 MHz or a Bruker ARX-400 spectrometer at 100.6 MHz, and ^{11}B NMR spectra were obtained on a Bruker ARX-500 spectrometer at 160.5 MHz. Proton chemical shifts were referenced to residual solvent protons, carbon chemical shifts were referenced to the solvent, and boron chemical shifts were referenced to external $BF_3{\cdot}OEt_2$. High resolution mass spectra were obtained at the UCLA mass spectroscopy facility using a VG AutoSpec instrument.

Synthesis of 1-(*tert*-Butyldimethylsilyl)-9,12-dimethyl-1,2-carborane (3b). The compound 9,12-dimethyl-*o*-carborane (7.16 g, 41.56 mmol) was dissolved in a benzene/diethyl ether mixture (2/1, 100 mL) and a 2.5 M solution of *n*-butyllithium in hexanes (18.33 mL, 45.71 mmol) was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h, after which *tert*-butyldimethylsilyl chloride (6.89 g, 45.71 mmol) was added at 0 °C. The solution was refluxed for 16 h, allowed to cool, and then washed with water (2 × 30 mL) and the water layers extracted with diethyl ether (50 mL). The combined organic layers were dried over magnesium sulfate and the solvent removed to yield **A** as a white waxy solid (11.88 g, 99%): ^{1}H NMR ($CDCl_3$) 3.24 (s, 1H, CH), 1.30−3.00 (br, 8H, BH), 1.02 (s, 9H, CCH_3), 0.22 (s, 6H, $SiCH_3$), 0.19 (br s, 6H, BCH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 57.0 (CSi), 53.5 (CH), 29.7 (*C*CH_3), 27.1 (C*C*H_3), 19.3 ($SiCH_3$), 1.1 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (CH_2Cl_2) 9.8, 7.8 (2 × 1B, BCH_3), −5.2 (2B), −10.7 (2B), −12.3 (2B), −14.6 (2B) ppm; HRMS (EI) for $C_{10}B_{10}H_{30}Si$ (*m/z*) calcd 286.3120, found 286.3117 (M^+).

Synthesis of 1,3-Bis(2′-(*tert*-butyldimethylsilyl)-9′,12′-dimethyl-1′,2′-carboranyl)propane (4b). Compound **3b** (5.34 g, 18.63 mmol) was dissolved in a benzene/diethyl ether solution (2:1, 100 mL) at 0 °C, and a 2.5 M solution of *n*-butyllithium in hexanes (7.45 mL, 18.63 mmol) was added dropwise. The mixture was warmed to room temperature over 30 min, and 1,3-dibromopropane (0.95 mL, 9.32 mmol) was added, after which the mixture was stirred at reflux overnight. Workup as for **3b** yielded an oily residue, which was carefully washed with pentane (3 × 30 mL) at 0 °C, leaving **4b** as a white solid (5.80 g, 51%): ^{1}H NMR ($CDCl_3$) 2.10 (t, 4H, CCH_2, J_{HH} = 8 Hz), 1.72 (m, 2H, CH_2), 1.04 (s, 18H, CCH_3), 0.80−3.00 (br, 16H, BH), 0.29 (s, 12H, $SiCH_3$), 0.19, 0.15 (br s, 2 × 6H, BCH_3) ppm; ^{13}C{^{1}H} NMR (C_6D_6) 73.6, 67.3 ($C_{carborane}$), 36.2 (*C*CH_2), 31.1 (CH_2), 27.4 (*C*CH_3), 26.8 (*C*CH_3), 20.2 ($SiCH_3$), 0.5 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (CH_2Cl_2) 10.8, 6.7 (2 × 2B, BCH_3), −4.7 (4B), −9.5 (8B), −11.3 (4B) ppm; HRMS (CI, NH_3) for $C_{23}H_{68}B_{20}NSi_2$ (*m/z*) calcd 630.6897, found 630.6922 $(M + NH_4)^+$.

Synthesis of 1,3-Bis(9′,12′-dimethyl-1′,2′-carboranyl)propane (5b). Compound **4b** (4.11g, 6.70 mmol) was dissolved in THF (60 mL) and cooled to −78 °C. A 1.0 M solution of tetrabutylammonium fluoride (13.4 mL, 13.4 mmol) was added slowly and the solution warmed to room temperature over 30 min. Water (20 mL) and diethyl ether (50 mL) were added and the water layer separated. After the water layer was washed with diethyl ether (2 × 50 mL), the combined organics were dried over anhydrous magnesium sulfate and reduced to dryness. The residue was dissolved in a small amount of diethyl ether/pentane (3:2) and chromatographed on a silica column. Elution with the same solvent mixture and removal of solvent yielded **5b** as a white solid (2.55 g, 99%): ^{1}H NMR ($CDCl_3$) 3.33 (br s, 2H, CH), 2.15 (t, 4H, CCH_2, J_{HH} = 8 Hz), 1.65 (m, 2H, CH_2), 1.10−3.20 (br, 16H, BH), 0.19, 0.16 (br s, 2 × 6H, BCH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 66.7 (*C*CH_2), 54.7 (CH), 36.2 (C*C*H_2), 29.1 (CH_2), 0.7 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (CH_2Cl_2) 7.3, 4.0 (2 × 2B, BCH_3), −7.5 (4B), −11.9 (4B), −13.5 (8B) ppm; HRMS (EI) for $C_{11}H_{36}B_{20}$ (*m/z*) calcd 384.4823, found 384.4833 (M^+).

Synthesis of Cyclic Tetramer 6a. To a solution of **5a**[10b] (0.50 g, 1.52 mmol) in THF (50 mL) at 0 °C was added 2.2 equiv of a solution of *n*-butyllithium (2.5 M in hexanes, 1.33 mL, 3.34 mmol) dropwise with stirring. The mixture was allowed to warm to ambient temperature. After additional stirring for 0.5 h, an excess of 1,3-dibromopropane (0.72 g, 3.56 mmol) was added *via* syringe at 20 °C. The resulting solution was heated under reflux for 16 h. After cooling, the reaction was quenched with 8−10 mL of H_2O. The aqueous layer was separated and the organic layer was washed with saturated NaCl and then dried over anhydrous magnesium sulfate. The solution was concentrated *in vacuo* to afford **6a** as a white powder, which was washed with diethyl ether and ethyl acetate and then dried under high vacuum. Recrystallization from hot DMA afforded pure **6a** (0.37 g, 66%). An additional 0.12 g of **6a** was obtained from the mother liquor bringing the total yield of **6a** to 87%: ^{1}H NMR (DMA-d_9) 2.94 (t, 16H, CCH_2, J_{HH} = 8 Hz), 2.11 (m, 8H, CH_2), 0.69−3.30 (br, 40H, BH) ppm; ^{11}B{^{1}H} NMR (DMA) 5.4 (8B), −10.6 (32B) ppm; EI-MS (*m/z*) 735.9 (M^+).

Synthesis of Cyclic Tetramer 6b. Compound **5b** (2.55 g, 6.63 mmol) was dissolved in THF (50 mL) at 0 °C, and a 2.4 M solution of *n*-butyllithium in hexanes (5.52 mL, 13.26 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h and then 1,3-dibromopropane (0.67 mL, 6.63 mmol) was added. The solution was refluxed for 16 h, and then the solvent was removed. The residue was dissolved in methylene chloride (300 mL) and washed with water (2 × 50 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered, and the filter cake was washed with THF (2 × 20 mL), which was added to the organic phase. Removal of solvent under reduced pressure yielded **6b** as a white solid (1.44 g, 51%): ^{1}H NMR ($CDCl_3$) 2.04 (t, 16H, CCH_2, J_{HH} = 8 Hz), 1.73 (m, 8H, CH_2), 0.90−3.00 (br, 32H, BH), 0.18 (br s, 24H, BCH_3) ppm; ^{13}C{^{1}H} NMR (THF-d_8) 72.4 (*C*CH_2), 33.9 (C*C*H_2), 28.6 (CH_2), 0.2 (vbr, BCH_3) ppm; ^{11}B{^{1}H} NMR (THF) 5.5 (8B, BCH_3), −8.3 (8B), −10.7 (24B) ppm; HRMS (EI) for $C_{28}H_{80}B_{40}$ (*m/z*) calcd 849.0273, found 849.0307 (M^+).

Synthesis of Cyclic Trimer 9. A solution of **8**[15] (5.00 g, 9.75 mmol) in THF (80 mL) at 0 °C was treated with 2 equiv of a solution of *n*-butyllithium (2.5 M in hexanes, 7.80 mL, 19.5 mmol) with stirring. The mixture was allowed to warm to ambient temperature. After 0.5 h a slight excess of 1,3-dibromopropane (0.98 mL, 9.80 mmol) was added dropwise. The resulting solution was heated under reflux for 8 h. After cooling, the THF solution was concentrated and 150 mL of diethyl ether was added and the reaction was quenched with H_2O (20 mL). The aqueous layer was separated and the organic layer was dried over anhydrous magnesium sulfate. The extract was concentrated *in vacuo* to afford **9** as a white powder, which was dried under high vacuum. Recrystallization from a mixture of methylene chloride/DMA afforded pure **9** (3.99 g, 74%). When the reaction was carried out in a mixture of benzene and diethyl ether (2:1), a yield of 63% was obtained, together with some insoluble material presumably polymeric in nature: ^{1}H NMR (acetone-d_6) 2.48 (m, 12H, CCH_2), 2.11 (m, 6H, CH_2), 0.69−3.30 (br, 30H, BH) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 80.5 (CB), 30.5 (CCH_2), 21.1 (CH_2) ppm; ^{11}B{^{1}H} NMR (acetone) 4.9 (6B), −10.1 (24B) ppm; EI-MS (*m/z*) 552.5 (M^+).

Synthesis of Cyclic Dimer 11a and Cyclic Tetramer 12. A solution of **10** (1.20 g, 3.04 mmol) in THF (110 mL) was treated with a solution of *n*-butyllithium (2.5 M in hexanes, 2.70 mL, 6.69 mmol) at 0 °C with stirring. During the course of the reaction the solution became yellow and then changed to red-orange after the addition of the *n*-butyllithium was complete. The mixture was allowed to warm to ambient temperature. After 1 h, α,α′-dibromo-*m*-xylene (0.88 g, 3.34 mmol) in THF (30 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 16 h and then was quenched with 5 mL of water and dried over anhydrous magnesium sulfate. The extract was filtered and concentrated *in vacuo* to half the original volume. A mixture of diethyl ether/ethyl acetate (1:1, 30 mL) was added at this point, and the solution was concentrated *in vacuo* to dryness. The solid material was washed with several portions of diethyl ether and dried under high vacuum. The material was then redissolved in a minimum amount of hot THF. Upon cooling and very slow evaporation of solvent in air, crystals of **12** were collected. Reduction of the mother liquor

(22) Kofron, W. G.; Baklawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(23) In all figures, boron atoms are represented as white spheres and carbon atoms are represented as black spheres.

and repeating this sequence twice afforded additional quantities of **12**. All the crude fractions of **12** were combined and recrystallized from the same solvent to afford pure **12** (0.54 g, 38%). Recrystallization of the residue from the combined mother liquors in hot ethyl acetate afforded pure **11a** (0.13 g, 9%). Characterization data for **11a**: ^{1}H NMR (acetone-d_6) 7.84 (s, 2H, C_6H_4), 7.31−7.46 (m, 6H, C_6H_4), 3.99 (s, 8H, CH_2), 0.80−3.00 (br, 20H, BH) ppm; ^{13}C{^{1}H} NMR (THF-d_8) 135.6, 132.9, 131.1, 128.1 (C_6H_4), 84.1 (CB), 39.8 (CH_2) ppm; ^{11}B{^{1}H} NMR (acetone) −5.1 (4B), −8.6 (8B), −12.4 (8B) ppm; HRMS (EI) for $C_{20}H_{36}B_{20}$ (*m/z*) calcd 492.4823, found 492.4800 (M^+). Characterization data for **12**: ^{1}H NMR (acetone-d_6) 7.38−7.43 (m, 12H, C_6H_4), 7.35 (s, 4H, C_6H_4), 3.94 (s, 16H, CH_2), 0.80−3.00 (br, 20H, BH) ppm; ^{11}B{^{1}H} NMR (THF) −4.8 (8B), −10.5 (32B) ppm; HRMS (negative ion FAB, NBA) for $C_{40}H_{72}B_{40}$ (*m/z*) calcd 984.9543, found 984.9560 $(M - H)^-$.

Synthesis of Cyclic Dimer 11b. A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.48 g, 3.33 mmol) in 50 mL of diethyl ether was treated with *n*-butyllithium (2.5 M in hexanes, 2.7 mL, 6.70 mmol) at 0 °C and stirred at room temperature for 3 h. To the resulting dilithiated carborane salt slurry was added α,α′-dibromo-*m*-xylene (0.88 g, 3.33 mmol) in diethyl ether (20 mL) at 0 °C. The mixture was then stirred at ambient temperature for 20 h. Lithium bromide was removed from the product solution by washing with brine, and the organic fraction was dried over anhydrous magnesium sulfate. After removal of the diethyl ether *in vacuo*, the residue was washed with pentane. The pentane-insoluble residue was recrystallized from hot benzene to yield **11b** as a white solid (0.59 g, 72%): ^{1}H NMR ($CDCl_3$) 7.22 (t, 2H, C_6H_4, J_{HH} = 8 Hz), 6.98 (d, 4H, C_6H_4, J_{HH} = 8 Hz), 6.66 (s, 2H, C_6H_4), 3.03 (s, 8H, CH_2), 1.45−3.35 (br, 20H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 136.8, 131.3, 129.1, 128.4 (C_6H_4), 75.9 ($C_{carborane}$), 43.2 (CH_2) ppm; ^{11}B{^{1}H} NMR (Et_2O) −5.9 (4B), −10.8 (12B), −14.9 (4B) ppm; HRMS (EI) for $C_{20}H_{36}B_{20}$ (*m/z*) calcd 492.4823, found 492.4812 (M^+).

Synthesis of Cyclic Dimer 11c and Cyclic Trimer 13. In a similar manner to the synthesis of **11b** above, a solution of *closo*-9,10-Me_2-1,7-$C_2B_{10}H_{10}$ (0.15 g, 0.87 mmol) in diethyl ether (30 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 0.70 mL, 1.74 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h, and then α,α′-dibromo-*m*-xylene (0.22 g, 0.85 mmol) in diethyl ether (20 mL) was added at 0 °C. The mixture was stirred at ambient temperature for 24 h and then washed with brine to remove lithium bromide. The organic portion was dried over anhydrous magnesium sulfate, then evaporated to dryness. The crude product was washed with cold pentane and then dissolved in a mixture of benzene and hexane (1:4) and chromatographed on flash silica gel. Careful elution with the same solvent mixture yielded first **11c** as a white solid after removal of solvent (0.16 g, 67%) and then **13** (0.04 g, 15%). Characterization data for **11c**: ^{1}H NMR ($CDCl_3$) 7.19 (t, 2H, C_6H_4, J_{HH} = 7 Hz), 6.96 (d, 4H, C_6H_4, J_{HH} = 7 Hz), 6.64 (s, 2H, C_6H_4), 2.98 (s, 8H, CH_2), 1.10−3.10 (br, 16H, BH), 0.33 (s, 12H, BCH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 137.0, 131.4, 129.0, 128.2 (C_6H_4), 73.2 ($C_{carborane}$), 43.1 (CH_2), −0.83 (CH_3) ppm; ^{11}B{^{1}H} NMR (Et_2O) −0.3 (4B, BCH_3), −4.4 (4B), −9.9 (8B), −19.0 (4B) ppm; HRMS (EI) for $C_{24}B_{20}H_{44}$ (*m/z*) calcd 548.5449, found 548.5427 (M^+). Characterization data for **13**: ^{1}H NMR ($CDCl_3$) 7.08 (t, 3H, C_6H_4, J_{HH} = 7 Hz), 6.90 (d, 6H, C_6H_4, J_{HH} = 7 Hz), 6.60 (s, 3H, C_6H_4), 2.90 (s, 12H, CH_2), 1.15−3.00 (br, 24H, BH), 0.30 (s, 18H, BCH_3), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 137.2, 131.5, 129.2, 128.0 (C_6H_4), 72.4 ($C_{carborane}$), 43.0 (CH_2), −1.2 (CH_3) ppm; ^{11}B{^{1}H} NMR (Et_2O) −0.4 (6B, BCH_3), −5.1 (6B), −10.6 (12B), −17.6 (6B) ppm; HRMS (EI) for $C_{36}B_{30}H_{66}$ (*m/z*) calcd 822.8174, found 822.8188 (M^+).

Synthesis of α,α′-Bis(2′-(*tert*-butyldimethylsilyl)-1′-1′,2′-carboranyl)lutidine (14). A solution of compound **3a** (2.58 g, 9.98 mmol) in a mixture of benzene and diethyl ether (1:1, 100 mL) at 0 °C was treated with a solution of *n*-butyllithium (2.0 M in hexanes, 5.5 mL, 11 mmol) and stirred for 30 min while warming to room temperature. α,α′-Dibromo-2,6-lutidine (1.59 g, 6.00 mmol) was slowly added to the mixture and the solution was stirred at room temperature for one day. After removal of solvent under reduced pressure, the residue was purified by chromatography on silica gel using a mixture of methylene chloride and pentane (1:3) as eluant. Removal of solvent yielded **14** as a white solid (1.86 g, 30%): ^{1}H NMR (acetone-d_6) 7.80 (t, 1H, C_5H_3N, J_{HH} = 8 Hz), 7.32 (d, 2H, C_5H_3N, J_{HH} = 8 Hz), 3.81 (s, 4H, CH_2), 1.2−2.8 (vbr, 20H, BH), 1.20 (s, 9H, CCH_3), 0.52 (s, 6H, $SiCH_3$) ppm; ^{13}C{^{1}H} NMR (acetone-d_6) 156.5, 138.5, 124.8 (C_5H_3N), 81.2 (CSi), 76.7 (CCH_2), 45.7 (CH_2), 28.1 (CCH_3), 21.1 (CCH_3), −2.1 ($SiCH_3$) ppm; ^{11}B{^{1}H} NMR (acetone) 0.9 (2B), −2.9 (2B), −6.7 (6B), −9.1 (10B) ppm; HRMS for $C_{23}H_{57}B_{20}NSi_2$ (*m/z*) calcd 623.5891, found 623.5916 (M^+).

Synthesis of α,α′-Bis(1′-1′,2′-carboranyl)lutidine (15). A solution of **3a** (0.14 g, 0.25 mmol) in THF (20 mL) was treated with a solution of tetrabutylammonium fluoride (1.0 M in THF, 0.6 mL, 0.6 mmol) at −78 °C and stirred for 30 min while warming to room temperature. The solvent was removed under reduced pressure, and then the residue was redissolved in a mixture of methylene chloride and pentane (1:4) and chromatographed on silica gel. Removal of solvent yielded **15** as a white solid (65 mg, 70%): ^{1}H NMR ($CDCl_3$) 7.72 (t, 1H, C_5H_3N, J_{HH} = 8 Hz), 7.15 (d, 2H, C_5H_3N, J_{HH} = 8 Hz), 3.82 (br s, 2H, CH), 3.63 (s, 4H, CH_2), 1.3−3.0 (vbr, 20H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 155.3, 138.5, 123.9 (C_5H_3N), 72.8 (CH), 59.0 (CCH_2), 45.1 (CH_2) ppm; ^{11}B{^{1}H} NMR (acetone) 0.5 (2B), −3.3 (2B), −7.1 (6B), −9.6 (10B) ppm; HRMS for $C_{11}H_{29}B_{20}N$ (*m/z*) calcd 391.4306, found 391.4315 (M^+).

Synthesis of α-Bromo-α′-(1′-1′,7′-carboranyl)lutidine (16). A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.50 g, 3.47 mmol) in diethyl ether (50 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 2.79 mL, 6.94 mmol) at 0 °C, then stirred for 3 h at room temperature. A solution of α,α′-dibromo-2,6-lutidine (0.92 g, 3.47 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C, and the mixture was stirred at ambient temperature for 24 h. The solution was washed with brine (2 × 40 mL) and the organic portion dried over anhydrous magnesium sulfate. Solvent was removed under reduced pressure and the product purified by chromatography on silica gel using a methylene chloride/pentane solvent mixture (1:2), yielding **16** as a white solid after removal of solvent (0.63 g, 55%): ^{1}H NMR ($CDCl_3$) 7.64 (dd, 1H, C_5H_3N, J_{HH} = 10,8 Hz), 7.33 (d, 1H, C_5H_3N, J_{HH} = 10 Hz), 7.01 (d, 1H, C_5H_3N, J_{HH} = 8 Hz), 4.52 (s, 2H, CH_2Br), 3.37 (s, 2H, CH_2), 2.87 (s, 1H, CH), 1.70−3.20 (br, 10H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 156.6, 156.4, 137.5, 123.5, 122.0 (C_5H_3N), 74.4 ($C_{carborane}$), 55.2 (CH), 44.6 (CH_2), 33.4 (CH_2Br) ppm; ^{11}B{^{1}H} NMR (Et_2O) −5.0 (1B), −8.4 (1B), −10.9 (4B), −13.9 (2B), −15.6 (2B) ppm; HRMS (EI) for $C_9B_{10}H_{18}BrN$ (*m/z*) calcd 328.2626, found 328.2620 (M^+).

Synthesis of α,α′-Bis(1′-1′,7′-carboranyl)lutidine (17). A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.20 g, 1.39 mmol) in a mixture of benzene and diethyl ether (2:1, 30 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 0.56 mL, 1.39 mmol) at 0 °C and then stirred at room temperature for 3 h. To this monolithiated carborane solution was added dropwise a solution of α,α′-dibromo-2,6-lutidine (0.18 g, 0.70 mmol) in diethyl ether at 0 °C, and the mixture was then stirred at reflux for 24 h. After cooling, the solution was washed with brine (2 × 40 mL), and the organic portion was dried over anhydrous magnesium sulfate and then purified by chromatography on silica gel (benzene/hexane, 1:4). Removal of solvent *in vacuo* yielded **17** as a white solid (0.14 g, 53%): ^{1}H NMR ($CDCl_3$) 7.62 (t, 1H, C_5H_3N, J_{HH} = 8 Hz), 7.03 (d, 2H, C_5H_3N, J_{HH} = 8 Hz), 3.36 (s, 4H, CH_2), 2.89 (s, 2H, CH), 1.40−3.20 (br, 20H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 156.4, 137.0, 122.9 (C_5H_3N), 74.7 ($C_{carborane}$), 55.2 (CH), 44.8 (CH_2) ppm; ^{11}B{^{1}H} NMR (Et_2O) −4.4 (2B), −9.9 (2B), −11.0 (8B), −13.9 (4B), −15.9 (4B) ppm; HRMS (EI) for $C_{11}B_{20}H_{29}N$ (*m/z*) calcd 391.4306, found 391.4299 (M^+).

Synthesis of 17 from 16. A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.10 g, 0.69 mmol) in a mixture of benzene and diethyl ether (2:1, 20 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 0.56 mL, 0.69 mmol) at 0 °C and stirred at room temperature for 3 h. To this monolithiated carborane solution was added a solution of **16** (0.23 g, 0.70 mmol) in diethyl ether (20 mL) dropwise at 0 °C. The mixture was then stirred under reflux for 24 h. Workup as described above yielded **17** (0.17 g, 62%).

Synthesis of 1,7-Bis(α′-bromo-α-lutidyl)-1,7-carborane (18). A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.18 g, 1.25 mmol) in THF (30 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 1.00 mL, 2.5 mmol) at 0 °C. After being stirred at room temperature for 3 h, the solution was cannulated dropwise into a solution of α,α′-dibromo-2,6-lutidine (0.65 g, 2.45 mmol) in THF (30 mL) at 0 °C. The mixture was heated at reflux for 6 h, and then 200 mL of diethyl ether was added. The solution was washed with brine (2 × 40 mL), and the organic portion

Table 1. Details of Crystallographic Data Collection

	6a	6b	11a	11b	11c	19
empirical formula	$C_{20}H_{64}B_{40}$	$C_{28}H_{80}B_{40}$	$C_{20}H_{36}B_{20}$	$C_{20}H_{36}B_{20}$	$C_{24}H_{44}B_{20}$	$C_{18}H_{30}B_{20}N_2$
fw	737.24	849.48	492.76	492.76	548.88	490.70
space group	$P\bar{1}$	$P2_1/a$	$C2/c$	$P2_1/n$	Pbca	Pcab
a (Å)	11.131(2)	13.500(2)	14.5682(8)	11.650(2)	12.532(2)	11.0428(6)
b (Å)	12.642(2)	31.141(3)	14.5046(8)	10.606(2)	14.271(2)	11.3785(6)
c (Å)	12.996(2)	13.831(2)	16.1998(8)	11.730(2)	18.143(3)	22.533(1)
α (deg)	84.383(6)					
β (deg)	65.884(6)	99.90(1)	95.631(2)	104.951(6)		
γ (deg)	97.292(5)					
V (Å^3)	1663	3889	3407	1400	3245	2831
Z	1	2	4	2	4	4
d_{calc} (g/cm^3)	1.10	1.06	1.07	1.17	1.12	1.16
radiation (λ)	Mo Kα (0.7107 Å)	Cu Kα (1.5418 Å)	Mo Kα (0.7107 Å)	Cu Kα (1.5418 Å)	Cu Kα (1.5418 Å)	Mo Kα (0.7107 Å)
μ (cm^{-1})	0.5	3.5	0.5	3.5	3.47	0.53
T (°C)	- 117	25	25	25	25	25
R[a]	0.079	0.097	0.081	0.069	0.076	0.074
R_w[b]	0.090	0.135	0.113	0.081	0.089	0.085

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$.

was dried over anhydrous magnesium sulfate. The solvent was removed and the residue redissolved in the minimum amount of a mixture of methylene chloride and pentane (2:3) and then chromatographed on flash silica gel. Elution with the same solvent mixture followed by removal of solvent *in vacuo* yielded **18** as a white solid (0.26 g, 41%): ^{1}H NMR ($CDCl_3$) 7.58 (dd, 2H, C_5H_3N, J_{HH} = 9,7 Hz), 7.30 (d, 2H, C_5H_3N, J_{HH} = 9 Hz), 7.03 (d, 2H, C_5H_3N, J_{HH} = 7 Hz), 4.38 (s, 4H, CH_2Br), 3.40 (s, 4H, CH_2), 1.60−3.30 (br, 10H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 156.7, 156.4, 138.0, 123.0, 121.7 (C_5H_3N), 74.7 ($C_{carborane}$), 44.8 (CH_2), 32.8 (CH_2Br) ppm; ^{11}B{^{1}H} NMR (Et_2O) −7.4 (2B), −10.2 (6B), −11.8 (2B) ppm; HRMS (EI) for $C_{16}B_{10}H_{24}Br_2N_2$ (*m/z*) calcd 512.2980, found 512.2976 (M^+).

Synthesis of Cyclic Dimer 19 from 18. A solution of *closo*-1,7-$C_2B_{10}H_{12}$ (0.07 g, 0.49 mmol) in THF (30 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 0.39 mL, 0.97 mmol) at 0 °C and stirred at room temperature for 3 h. A solution of **18** (0.25 g, 0.49 mmol) in THF (30 mL) was slowly added at 0 °C. The mixture was heated under reflux for 14 h, and then diethyl ether (200 mL) was added to the reaction mixture. The organic phase was washed with brine (100 mL), and then dried over anhydrous magnesium sulfate. Chromatography on flash silica gel with a solvent mixture of benzene and hexane (1:1) and removal of solvent *in vacuo* yielded **19** as a white solid (0.20 g, 84%): ^{1}H NMR ($CDCl_3$) 7.57 (t, 2H, C_5H_3N, J_{HH} = 8 Hz), 7.01 (d, 4H, C_5H_3N, J_{HH} = 8 Hz), 3.24 (s, 8H, CH_2), 1.60−3.50 (br, 20H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 156.0, 136.8, 123.2 (C_5H_3N), 74.1 ($C_{carborane}$), 45.3 (CH_2) ppm; ^{11}B{^{1}H} NMR (Et_2O) −5.2 (4B), −10.2 (12B), −14.3 (4B) ppm; HRMS (EI) for $C_{18}B_{20}H_{34}N_2$ (*m/z*) calcd 494.4728, found 494.4722 (M^+).

Synthesis of 19 from 17. A solution of **17** (0.09 g, 0.23 mmol) in THF (25 mL) was treated with *n*-butyllithium (2.5 M in hexanes, 0.18 mL, 0.46 mmol) at 0 °C and stirred at room temperature for 3 h. To this solution was added slowly a solution of α,α′-dibromo-2,6-lutidine (0.06 g, 0.23 mmol) in THF (30 mL) at 0 °C. The mixture was gently refluxed for 24 h, and then 200 mL of diethyl ether was added. Workup as above yielded **19** as a white solid (0.07 g, 58%).

Synthesis of Cyclic Amine Oxide Dimer 20. A solution of **19** (0.10 g, 0.20 mmol) in methylene chloride (20 mL) was treated with 3-chloroperoxybenzoic acid (0.07 g, 0.40 mmol) and stirred for 24 h. The reaction mixture was washed with brine (3 × 80 mL) and then dried over anhydrous magnesium sulfate. Removal of the solvent yielded **20** as a white solid (0.08 g, 79%): ^{1}H NMR ($CDCl_3$) 7.57 (t, 2H, C_5H_3NO, J_{HH} = 8 Hz), 7.01 (d, 4H, C_5H_3NO, J_{HH} = 8 Hz), 3.35 (s, 8H, CH_2), 1.60−3.50 (br, 20H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) 157.9, 137.0, 124.1 (C_5H_3NO), 75.1 ($C_{carborane}$), 45.9 (CH_2) ppm; ^{11}B{^{1}H} NMR (Et_2O) −5.0 (4B), −10.4 (12B), −13.8 (4B) ppm; HRMS (EI) for $C_{18}B_{20}H_{34}N_2O_2$ (*m/z*) calcd 526.4626, found 526.4605 (M^+).

Structure Determinations. An abbreviated set of crystal data is given in Table 1. All other details and results of the six structure determinations are offered as Supporting Information.

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Supporting Information Available: For compounds **6a, 6b, 11a, 11b, 11c,** and **19**, text giving experimental details of crystallographic data collection, solution, and refinement, tables of bond distances and angles, and positional and thermal parameters, and figures showing the atom-numbering system used (57 pages). See any current masthead page for ordering information and Internet access instructions.

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