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Camouflaged Carborarods Derived from *B*-Permethyl-1,12-diethynyl-*para*- and *B*-Octamethyl-1,7-diethylnyl-*meta*-carborane Modules

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Abstract: Rigid camouflaged carborarods constructed from the corresponding *C*,*C*′-diethynyl derivatives of *B*-decamethyl-1,12-dicarbadodecaborane(12) (**6**) and *B*-octamethyl-1,7-dicarbadodecaborane(12) (**48**) have been synthesized by largely conventional organic transformations. These carborarods are the longest discrete rod species available by this method in which B-methylated *p*-carborane and *m*-carborane cages are linked through their carbon vertices by using butadiynylene moieties. They exhibit enhanced solubility in common organic solvents relative to all other presently known carborane-based rigid-rod molecules. The oxidative coupling of bis(ethynyl) derivatives of **6** generates oligomers containing, on average, 16 carborane modules. The structural characterization of the corresponding dimeric species revealed that the carborarods possess a sinusoidal chain distortion in the solid state. The stereoelectronic properties of these and related model carborarods were evaluated by using molecular dimensions as a monitor for the comparison of computational and experimental methods. In addition, the effect of exhaustive B-methylation of 12- and 10-vertex *para*-carborane cages in a series of model *C*,*C*′-diethynyl derivatives was similarly investigated by computational and structural studies. As expected, a correlation of intercage C−C bond lengths with cage size was observed and was attributed to hybridization effects. B-Permethylation had no significant structural effect with either 10- or 12-vertex cage derivatives. Relative to unsubstituted compounds, thermal and chemical stabilities of B-permethylated derivatives were increased through the operation of a steric “bumper-car” process, and solubilities in organic solvents were enhanced. The formation of linear, sterically encumbered platina–carborarods using ethynyl derivatives of **6** as precursors is described.

Keywords: alkynes • boranes • carboranes • carborarods • rigid rods

Introduction

In recent years, efforts to synthesize rigid-rod molecules of defined lengths[1] for use as molecular building blocks (MBBs) in nanoarchitectural, nanomechanical, and supramolecular constructs[2] has increased dramatically. Among the potential applications for such assemblies, nanomachine construction, the functionalization of surfaces, and the creation of molecular electronic devices[2,3] are the most promising. The assembly of such arrays in a “bottom-up” approach[3a] involves the assembly of tailor-made MBBs. Consequently, a large selection of available MBBs would be useful to the nano- or molecular-device architect.

The three icosahedral carborane isomers (*ortho*-, *meta*-, and *para*- or 1,2-, 1,7-, and 1,12-, respectively) as well as their 10-vertex homologues meet all criteria to function as core modules in macromolecular scaffolds.[4] The chemistry at both their CH and BH vertices is well described, they exhibit excellent thermal and photochemical stabilities, and more significantly, their varied geometries provide precise directional control of *exo*-polyhedral bond formation. For instance, the linkage of *para-closo*-$C_2B_8H_{10}$ (1,10-carborane) or *para-closo*-$C_2B_{10}H_{12}$ (1,12-carborane) cages together at their antipodal carbon vertices (1,10- and 1,12-substitution, respectively) leads to the nearly linear so-called carbora-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains tables listing atomic coordinates, temperature factors, bond lengths and angles, torsion angles, and details of the refinement of the X-ray crystallographic data for **30** (34 pages), **40** (11 pages), and **41** (16 pages).

rods.[5] Investigations that explore the suitability of such species as MBBs have focused on both the 10- and 12-vertex *para*-carborane precursors. UV-visible spectroscopic studies with 1,12-bis(aryl) derivatives of the latter were conducted by Mingos et al.[6] and Wade and co-workers.[7] Derivatives of 1,12-carborane bearing sigma-bonded metal centers at their carbon vertices have been examined by Hawthorne and collaborators[8] and Low et al.[9] by using electrochemical methods. All of these investigations have shown that electronic effects can be transmitted transversely through the icosahedral 1,12-carborane cage. However, related experimental and computational studies with 10-vertex 1,10-carborane derivatives by Kaszynski et al.[10] suggested that the bicapped Archimedian antiprismatic cage possesses the ability to form more effective C_{cage}–C π bonds to unsaturated *exo* substituents than those observed with the corresponding 1,12-carborane module. These studies included the ethynyl-substituted carborarod compounds 12,12′-bis(1-heptynyl)-1,1′-bis(1,12-carborane) (**1**) and 10,10′-bis(1-heptynyl)-1,1′-bis(1,10-carborane) (**2**) (Figure 1).[10a,b] This finding was complemented by theoretical analyses by Allis and Spencer.[11] Parallel to studies involving *para*-carboranes, electron tunneling through icosahedral *ortho*-carborane clusters was detected at ambient temperature by using scanning tunneling microscopy (STM) techniques.[12]

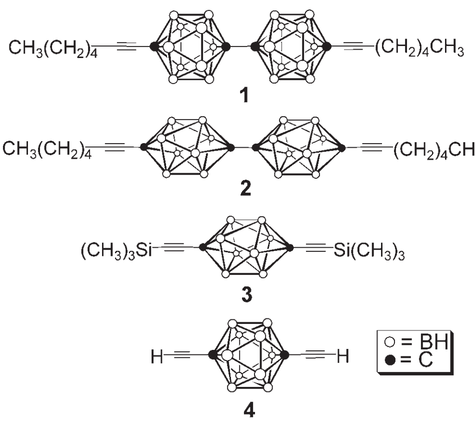


Figure 1. Previously studied *C*,*C*′-bis(alkynyl)-*para*-carborane derivatives.

Rigid carborarods derived from 10- and 12-vertex *para*-carboranes represent attractive candidate MBB structures, but several factors have complicated their syntheses. The yields of coupling reactions of carboranes and alkynes are typically modest. For instance, the palladium-mediated syntheses of 1,10-bis(trimethylsilylethynyl)-1,10-$C_2B_8H_8$ (**3**)[10c] and 1,12-bis(ethynyl)-1,12-carborane (**4**)[13] (Figure 1) afforded the corresponding products in 26 and 15 % yields, respectively. Such low yields are unattractive considering the high cost of commercially available carborane precursors. Also, the intrinsically poor solubility of carborarods in organic solvents prevents their extension in length or further coupling to form other structures. Tetra(1,12-carborane)-1,12‴-H_2-(1,12-$C_2B_{10}H_{10}$-1,12-ylene)$_4$ (**5**)[5a] serves as an extreme example. The terminally (1,12‴) disubstituted bis[tri(*n*-hexyl)silyl] derivative of **5** is easily soluble in hydrocarbons,[5a] but **5** itself is intractable in all common solvents. Consequently, all attempts to further functionalize **5** at its BH or CH vertices have failed. The introduction of rigid organic linkers between cages did not markedly change the solubility of the corresponding carborarods. Several dimeric dumbbell-shaped rods containing two icosahedral carborane cages have been described which utilize biphenylene,[5d,14] phenylene,[5f,15] ethynylene,[5c] butadiynylene,[5c,16] staffanylene,[17] and mercury[8,18] as interconnections. A trimeric, icosahedral 1,12-carborane-containing rod linked by ethynylene units and having terminal iodine substituents represents, to date, the longest rigid carborarod *in this category* composed of more than two icosahedra.[5c]

Sacrificing the rigidity of the linker makes it possible to generate carborane-containing polymers with molecular weights of $>10^5$ dalton[19] from soluble intermediates. However, one may retain the rigidity of a macromolecular structure and enhance its solubility by attaching bulky hydrophobic (or hydrophilic) substituents to individual repeating units.[1]

Recently, members of our laboratory developed the concept of camouflaged carboranes[4f,20] which provided methods leading to the syntheses of a *B*-permethylated 1,12-carborane (**6**) and 4,5,6,8,9,10,11,12-octamethyl-*m*-carborane (**48**) as well as many related species.[20a,d] The solubilities of such compounds and their derivatives in common organic solvents, as well as their stabilities towards aggressive reagents such as bases in protic media, are increased compared to their non-methylated counterparts. In developing pathways to larger rigid rods derived from **6** and **48**, camouflaged carborarod intermediates with improved solubilities in common organic solvents were required in order to reach carborarod lengths beyond those of truncated carborarods containing only two icosahedra. In addition, for reactions which normally lead to decomposition, the presence of bulky B–CH_3 vertices as neighbors to sensitive linker groups, such as those containing -C≡C-, should improve the kinetic stability of the species as a result of the steric encumbrance. This may be described as the "bumper-car" effect. Lastly, the electronic effects of B-permethylation of 10- and 12-vertex carborane structures were investigated. The only related study of such effects was that of King and Michl et al.[21a] on the consequence of B-permethylation of the $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ ion and the discovery of the $[closo\text{-}B_{12}(CH_3)_{12}]^{2-}$ ion by Peymann and Hawthorne.[21b] Electronic spectra and electrochemical and computational studies proved the *B*-methyl-group substituent to be electron-releasing through hyperconjugation.[21] Striking evidence for this electronic effect is found in the ease with which $[closo\text{-}CB_{11}H_{12}]^-$ and $[closo\text{-}B_{12}(CH_3)_{12}]^{2-}$ are converted to the corresponding neutral and singly charged[21b] radicals, respectively, by reversible one-electron oxidation. Evidence for a similar substituent effect was sought in the present study through the use of X-ray diffraction studies, electronic spectroscopy, nuclear magnetic resonance spectroscopy, and computations at the Hartree–Fock/6-31G* level of theory.

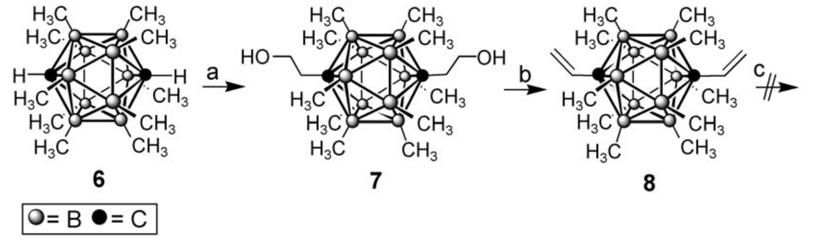
Results and Discussion

Synthesis of B-permethylated 1,12-carborarods: The nature of the linkage used to connect two cages of **6** is governed by the limited reactivity of the CH vertices that are immersed in the encumbering steric environment created by their surrounding methyl groups. As expected, direct copper-mediated homocoupling of **6** failed. In order to place an ethynyl linker substituent at the 1-position, the cross-coupling reaction of **6** with iodo(trimethylsilyl)acetylene and the similar reaction of the 1-iodo derivative of **6** with trimethylsilylacetylene were both examined under Sonogashira and Stevens–Castro conditions.[22] However, instead of the desired 1-trimethylsilylethynyl derivative of **6**, the formation of bis(trimethylsilyl)butadiyne was observed in both cases. Consequently, an alternative synthetic route to ethynyl-substituted **6** was developed.

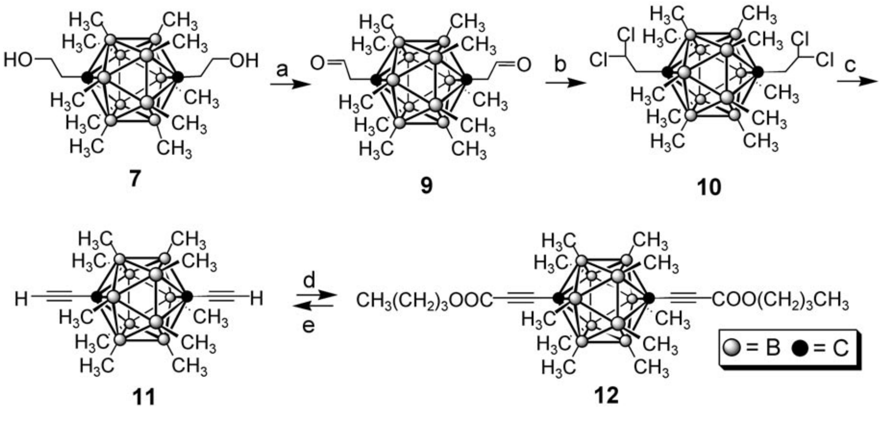
Recently, a method for preparing *C*-hydroxyalkyl derivatives of **6** in high yields was reported,[23] which provides an attractive route to useful carborarod precursors. The 1,12-bis(2-hydroxyethyl) derivative **7**, prepared in a 65 % yield by the reaction of 1,12-dilithiated **6** and ethylene oxide, was used as the precursor to the corresponding bis(ethynyl) derivative. Initially, diol **7** was dehydrated to the corresponding bis(vinyl) derivative **8** by treatment with Al(O*i*Pr)$_3$ at 300 °C.[24] The subsequent addition of bromine to the vinyl groups was expected to provide a suitable precursor which, upon dehydrobromination, would yield the desired acetylene. However, only unreacted starting material was recovered from the reaction of **8** with bromine, even in the presence of Lewis acids (Scheme 1).

Starting from diol **7**, an alternative pathway was probed which involved an oxidation–halogenation–elimination sequence. Due to the poor solubility of diol **7** in all common organic solvents, its oxidation to the corresponding dialdehyde **9** was best carried out under Parikh–Doering conditions[25] by using a mixture of DMSO and dichloromethane as the reaction medium (Scheme 2). This method provided **9** in yields ranging from 65 to 75 %. Compound **9** was chlorinated with PCl$_5$[26] to yield 1,12-bis(2,2-dichloroethyl) derivative **10** in a 75 % yield. Finally, dehydrochlorination of **10** with NaNH$_2$ in liquid ammonia[26,27] gave the desired 1,12-bis(ethynyl) derivative **11**. Crude **11** contained minor impurities, which were spectroscopically identified as vinyl derivatives of **6**. The purification of **11** was carried out by converting it to the corresponding 1,12-bis(*n*-butyl propiolyl) diester **12** which was purified by using flash column chromatography on silica gel. Deprotection of **12** following the procedure of Eschenmoser[28] gave pure **11** (Scheme 2). The yield of **11** (non-optimized) over all steps was 25–30 % and consequently unsatisfactory for extensive carborarod synthesis.

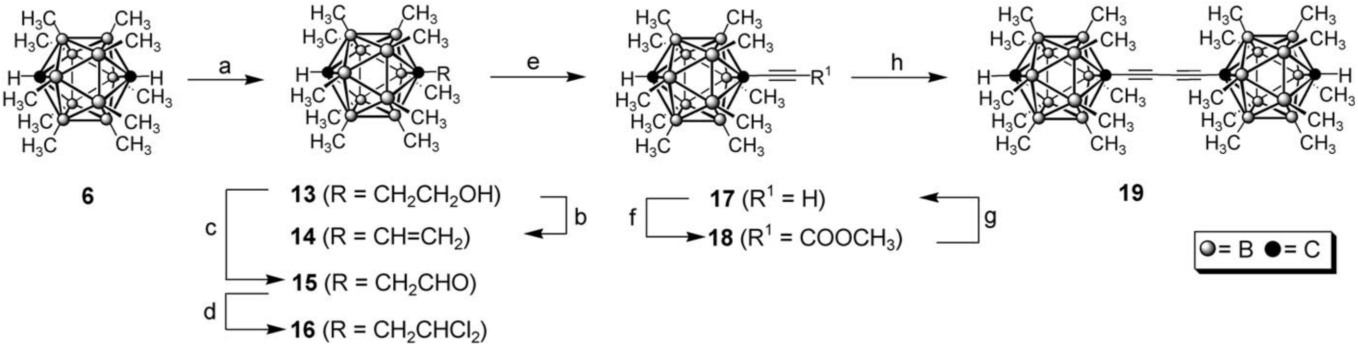
An alternative strategy that employed the 1-ethynyl derivative of **6**, that is, compound **17**, as the primary rod-building module, was investigated. This 1-ethynyl derivative was synthesized from **6** in four steps (Scheme 3). The reaction of monolithiated **6** with ethylene oxide gave the 1-(2-hydroxyethyl) derivative **13** in a 94 % yield. Alcohol **13** was converted to the corresponding vinyl derivative **14** in a 61 % yield. Bromination of **14** produced an intractable mixture of products. As an alternative route, alcohol **13** was quantitatively converted to the corresponding aldehyde **15** by using the Swern procedure,[29] and the subsequent reaction of **15** with PCl$_5$ provided the 1-(2,2-dichloroethyl) derivative **16** in a 85 % yield. Treatment of **16** with *n*BuLi[30] at low temperature afforded acetylene **17**, but in only a 15 % yield. Major



Scheme 1. Synthesis of bis(vinyl) precursor **8**. a) CH$_3$Li, ethylene oxide; b) Al(O*i*Pr)$_3$, 300 °C; c) Br$_2$, HgBr$_2$.



Scheme 2. Synthesis of 1,12-bis(ethynyl) derivative **11**. a) SO$_3$·py (py = pyridine), DMSO, CH$_2$Cl$_2$; b) PCl$_5$; c) NaNH$_2$, NH$_3$; d) *n*BuLi, ClCOO*n*Bu; e) 2,6-lutidine, LiI.

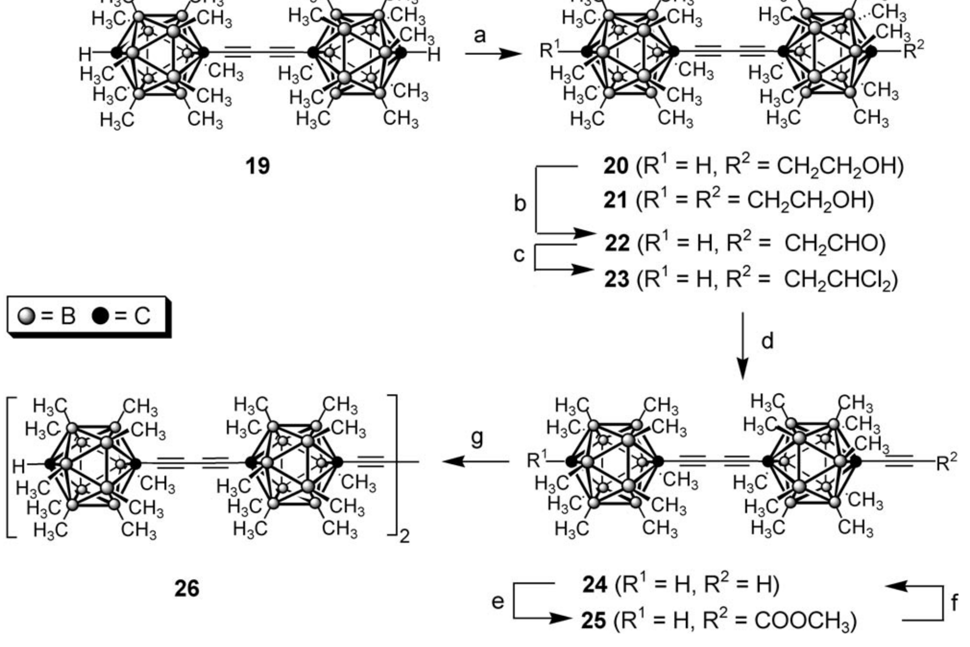


Scheme 3. Synthesis of 1,1′-(1,4-butadiyne) rod **19**. a) CH_3Li, ethylene oxide; b) $Al(OiPr)_3$, 300 °C; c) $(COCl)_2$, DMSO, iPr_2NEt; d) PCl_5; e) $NaNH_2$, NH_3; f) *t*BuLi, $ClCOOCH_3$; g) 2,6-lutidine, LiI; h) CuCl, O_2, py, DBU, 45 °C, 2 h.

byproducts were the hex-2-enyl and chlorovinyl derivatives of **6**. The desired product **17** was therefore obtained in an 88 % yield by dehydrochlorination of **16** using $NaNH_2$ in liquid ammonia. As observed in the formation of **11**, partial reduction occurred and vinyl compound **14** was generated as the major byproduct in about a 5 % yield. The removal of **14** from **17** was achieved by converting **17** to **18**, separation of **18** from **14** by chromatography, and regeneration of **17** from pure **18**. Finally, oxidative coupling of alkyne **17** under Glaser conditions[31] furnished the 1,1′-(1,4-butadiyne) rod **19** in a quantitative yield (Scheme 3). The highest overall yield of **19** obtained was 66 %.

The dimeric rod **19**, which has excellent solubility in hydrocarbon solvents, exhibits a melting point of nearly 400 °C thereby demonstrating high thermal stability. Furthermore, **19** proved to be quite chemically inert. The butadiynylene linkage could be neither brominated (Br_2 or BBr_3) nor reduced (PtO_2/H_2 or $LiAlH_4$). Also, it was impossible to convert **19** into a thiophene or pyrrole derivative.[32] However, fluorination of **19** with elemental fluorine (10 % in N_2) led to the rupture of the diyne moiety.[33] The reaction sequence developed for the synthesis of **17** was repeated beginning with **19** (Scheme 4). Lithiation of **19** and subsequent reaction with ethylene oxide led to the desired mono(2-hydroxyethyl) derivative **20** in a 60 % yield. Both unreacted **19** (20 %) and the 12,12′-bis(2-hydroxyethyl) derivative **21** (20 %) could be easily separated from **20** by using column chromatography. Oxidation of **20** (Swern) followed by chlorination (PCl_5) produced the 12-(2-oxoethyl) and the 12-(2,2-dichloroethyl) derivatives **22** and **23**, respectively. Dehydrochlorination of **23** provided crude 12-ethynyl derivative **24**, which was purified through its transformation to the 12-(methyl propiolyl) derivative **25**, followed by chromatography on silica gel and deprotection (vide infra). Alkyne coupling of **24** (Glaser) provided the colorless, tetrameric rod **26** in a 94 % yield.

In contrast to dimeric rod **19**, the solubility of **26** in hexanes is poor and its dissolution requires the use of hot benzene. Satisfactory ^{13}C NMR data for **26** could be acquired by using deuterated aromatic solvents at elevated temperatures. Further functionalization of **26** at its terminal CH vertices was attempted by lithiation with *n*BuLi in Et_2O/benzene. Surprisingly, no reaction of the dilithio derivative of **26** (12,12′-Li_2 **26**) was observed with ethylene oxide or methyl formate. However, upon addition of D_2O, 12,12′-D_2 **26** was isolated thus demonstrating that deprotonation of both the



Scheme 4. Synthesis of tetrameric rod **26**. a) CH_3Li, ethylene oxide; product distribution **19**/**20**/**21** = 1:3:1; b) $(COCl)_2$, DMSO, iPr_2NEt; c) PCl_5; d) $NaNH_2$, NH_3; e) *t*BuLi, $ClCOOCH_3$; f) 2,6-lutidine, LiI; g) CuCl, O_2, py, DBU, 45 °C, 2 h.

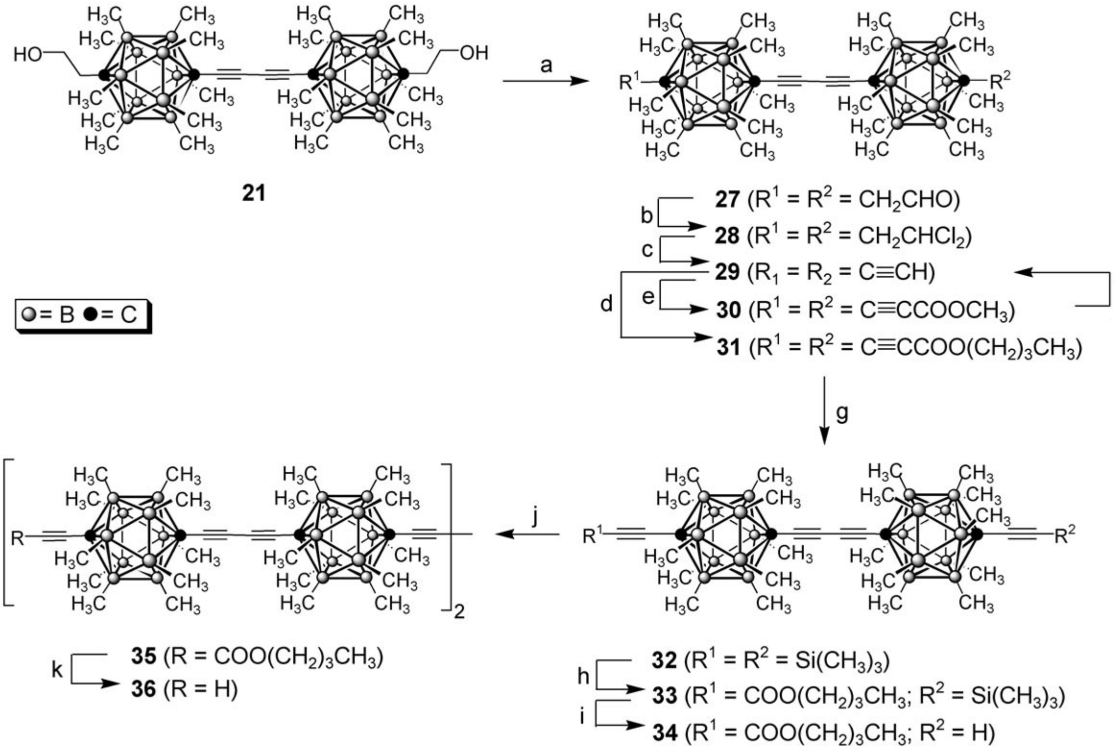
terminal CH vertices of **26** had occurred. Apparently, the nucleophilicity of the terminal carbanionic centers present in 12,12′-Li_2 **26** is effectively reduced compared with the analogous dianion of its dimeric counterpart **19**. This finding might be explained as a result of aggregation of the dilithio reagent.

As continued stepwise lengthening of the oligomer using the newly developed methods proved to be impossible, the rod synthesis was modified such that the terminal alkyne substituents to be attached to **26** were introduced prior to the final coupling step (Scheme 5). Thus, diol **21** was oxidized to aldehyde **27** which produced **28** upon chlorination. Treatment of **28** with $NaNH_2$ in NH_3 gave the corresponding crude 12,12′-bis(ethynyl) derivative, compound **29**. The purification of **29** was accomplished by its conversion to the corresponding 12,12′-bis(methyl propiolyl) derivative **30** as described earlier. The monoprotection of **29** with *n*-butyl chloroformate failed due to precipitation of its bis-lithiated derivative and instead 12,12′-bis(*n*-butyl propiolyl) rod **31** and unreacted **29** were isolated. Following the procedure of Holmes et al.,[34] Li_2 **29** was treated with $(CH_3)_3SiCl$ to give the bis(trimethylsilyl) derivative **32** which, after reaction with one equivalent of $CH_3Li{\cdot}LiBr$ and subsequent treatment with *n*-butyl chloroformate, produced carborarod **33** in a 47% yield. Desilylation of **33** was accomplished by using $KF{\cdot}2H_2O$ in DMF[35] to produce the corresponding 12-(*n*-butyl propiolyl)-12′-ethynyl derivative **34** in a quantitative yield. Compound **34** was oxidatively coupled to afford the hexane-soluble derivative 12,12′-bis(*n*-butyl propiolyl) **35**. Removal of the ester functions of **35** afforded the corresponding bis(ethynyl) derivative, compound **36** in a 98% yield (Scheme 5).

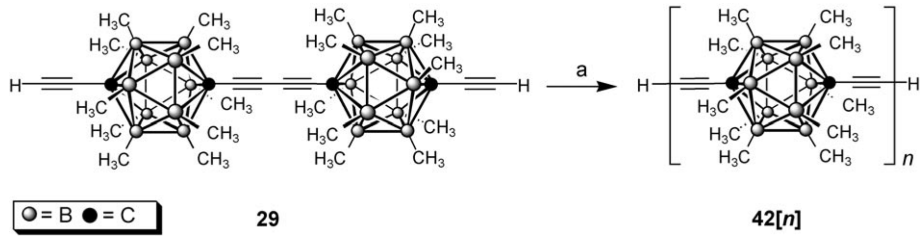
Derivatization of rod **36**, which is significantly more soluble in hydrocarbon solvents than rod **26**, was attempted by placing bulky trialkylsilyl groups at the ethynyl-group termini. However, no reaction took place upon treatment of bis-lithiated **36** (CH_3Li) with R_3SiCl (R = *n*Bu, *n*Hex) in Et_2O, even in the presence of tetramethylethylenediamine (TMEDA). Copper(I)-mediated coupling reactions of the terminal ethynyl groups of **36** are under investigation.

Synthesis of B-permethylated 1,12-carborarod oligomers: In order to determine the maximum number of *para*-carborane cages which could be assembled by using the diyne linkage formed by Glaser oxidation, the polymerization of bis(ethynyl) derivative **29** was investigated.

Bis(alkyne) **29** was coupled as described in Scheme 6. This oligomerization reaction resembles the corresponding reaction of 1,4-diethynylbenzene conducted by Hay.[36] The resulting mixture of oligomers was extracted with hot toluene and filtered through a short bed of silica gel without loss of material (determined by mass balance). Removal of toluene solvent afforded hexane-insoluble and slightly yellow polymer **42[*n*]** with a melting or decomposition point that exceeds 350 °C. This should be compared with the rapid decomposition at 100 °C of the polymer resulting from the



Scheme 5. Synthesis of bis(ethynyl) tetrameric rod **36**. a) $(COCl)_2$, DMSO, *i*Pr_2NEt; b) PCl_5; c) $NaNH_2$, NH_3; d) CH_3Li, ClCOO*n*Bu; e) *t*BuLi, $ClCOOCH_3$; f) 2,6-lutidine, LiI; g) CH_3Li $(CH_3)_3SiCl$; h) $CH_3Li{\cdot}LiBr$, ClCOO*n*Bu, product distribution **31**/**32**/**33** = 1:1:2; i) $KF{\cdot}(H_2O)_2$, DMF; j) CuCl, O_2, DBU, py, RT, 8 h; k) 2,6-lutidine, LiI.



Scheme 6. Polymerization of **29** to **42**. a) CuCl, O$_2$, py, DBU, 45 °C, 5 h; $n_{\text{average}} = 16$.

coupling of 1,4-diethynylbenzene.[36a] As expected, the ^{11}B NMR spectrum of **42[*n*]** closely resembles that of **26** and **36**, exhibiting a broad singlet. The ^{1}H NMR spectrum of a specimen dissolved in [D$_8$]toluene at 67 °C displayed the signals expected for the methyl ($\delta = 0.09$–0.00 ppm) and acetylenic protons ($\delta = 1.96$ ppm). Their integration ratio suggested an average number of 16 cages per mole to be present in the oligomer. Based on the structural data obtained from **30** and **41**, the length of a rigid rod consisting of 16 *p*-carborane cages, 15 diynylene linkers, and 2 terminal ethynyl groups is 156 Å with a calculated molecular weight of 5285 dalton.

Unfortunately, MALDI-TOF data for **42[*n*]** that would complement the NMR results could not be obtained. Furthermore, attempts to separate the mixtures of oligomers by using gel-permeation chromatography failed. However, it is evident that the incorporation of B-permethylated 1,12-carborane cages provides increased solubilities commensurate with oligomer chain lengths, which far exceed the length of the oligomer formed from the phenyl–phenyl coupling of 1,12-di(*p*-chlorophenyl)-1,12-carborane with Zn and [Ni(PPh$_3$)$_4$] (Figure 2). The latter was reported to have a relatively low degree of polymerization due to the precipitation of insoluble short-chain oligomers formed during the synthesis.[5d]

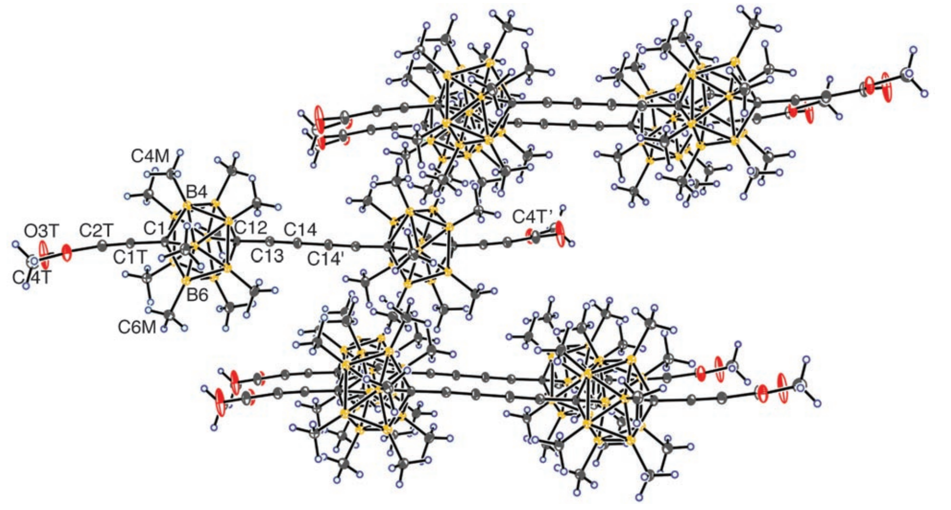


Figure 3. Crystal packing in **30** shown by five of the centrosymmetric rod molecules. Selected molecular parameters: C14–C14′ 1.370(4), C13–C14 1.197(3), C13–C12 1.437(3), C1–C1T 1.440(3), C1T–C2T 1.189(3), C4T–C4T′ 24.506(8), B6–C6M 1.582(4), B4–C4M 1.573(3), C1–B4 1.719(4), C1–B6 1.731(3) Å; C14′-C14-C13 179.6(4), C14-C13-C12 176.7(3), C1-C1T-C2T 176.3(3), C1-C12-C13 178.7(2), C12-C13-C14-C14′ 172(4)°.

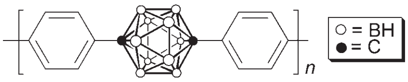


Figure 2. Poly(4,4′-biphenylene-1,12-dicarbadodecaborane).

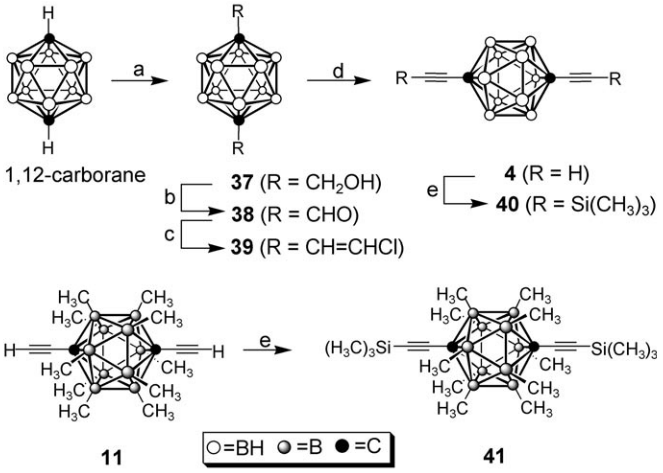
Structure of *para*-carborarods: Determination of the structural features of the butadiyne linkage present in *para*-carborarods has been restricted to the study of the dimer, **30**, due to the limited availability of suitable crystals of X-ray quality of other compounds with a butadiyne linker array. The presence of terminal carboxymethyl groups in **30** should not affect the bond lengths present in the internal diyne linkage of this species.

The structure of **30** (Figure 3) obtained at 100 K[37] displayed a sinusoidal distortion of the rod. A similar distortion had previously been found in *closo*-1,1′-bis(12″-phenyl-1″,12″-carboran-1″-yl)-4,4′-biphenylene[5d] which was attributed to crystal-packing forces. In contrast to the solid-state structure of the latter species, the molecules of **30** in the crystal are present as parallel layers in a hexagonally close-packed assembly of cages apparently mediated by van der Waals forces between the *B*-methyl groups. The distance between the terminal acetylenic carbon atoms is 20.86 Å; thus the length of the related tetrameric structure **36** would be approximately 42 Å. The inner and outer C_{cage}–C_{ethynyl} bonds in **30** (1.437(3) and 1.440(3) Å, respectively) both appear in the short range of C(sp^2)–C(sp) bonds seen in typical analogues (1.434 Å).[38] Figure 3 presents selected bond lengths and angles for **30**.

Methylated models for *para*-carborarods: In order to experimentally assess the electronic and stereochemical consequences of exhaustive B-methylation of carborane cages in *para*-carborarods, as described below, appropriate model species **4** and its trimethylsilyl derivative, **40**, were required for study along with their B-permethylated counterparts, **11** and **41**, respectively.

Compound **40** was previously reported by Batsonov[13] and Kaszynski et al.[10f] and was produced in a low yield

(15%) from the Cadiot–Chodkiewicz coupling of *C*,*C′*-dicopper-1,12-carborane and bromo(trimethylsilyl)acetylene. The former authors desilylated **40** to form **4** which they structurally characterized,[13] while Kaszynski[10f] and co-workers carried out an X-ray diffraction study of **40**. A significantly improved overall yield of **4** (64%) has been achieved by using the four-step synthesis outlined in Scheme 7, analogous to the synthesis of **11** described in Scheme 2. The desired **40** and **41** were obtained by trimethylsilylation of **4** and **11**, respectively.



Scheme 7. Synthesis of model compounds **11** and **41** for computational studies. a) *n*BuLi, $(CH_2O)_n$; b) SO_3·py, DMSO; c) $(Ph_3PCH_2Cl)Cl$, KO*t*Bu; d) *n*BuLi; e) CH_3Li, $(CH_3)_3SiCl$.

Single crystals of **41** suitable for X-ray diffraction studies[39] were obtained from solutions of the crystals in pentane. The structure of **41** (Figure 4) revealed the presence of weak intermolecular hydrogen bonds in which trimethylsilyl hydrogen atoms interact with silicon atoms (average $SiCH_2$–H···Si 4.35(18) Å). The structure determination of **11** proved to be impossible due to disorder in the crystal at 100 K.

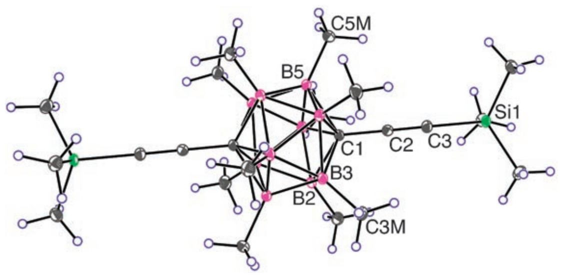


Figure 4. Ortep representation of **41**. Selected molecular parameters: C1–C2 1.4465(18), C2–C3 1.2023(19), C3–Si1 1.8447(14), B2–C1 1.7255(19), B2–B3 1.797(2) Å; C3-C2-C1 177.93(15)°.

Electronic and stereochemical effects of carborane cage size, B-methylation, and terminal trimethylsilylation of *C*-ethynyl substituents: As pointed out in the Introduction, the results of previous studies[10] suggest that the 12-vertex *closo*-1,12-$C_2B_{10}H_{10}$-1,12-ylene module is less efficient as a π-bonding module than its divalent *closo*-1,10-$C_2B_8H_8$-1,10-ylene counterpart when attached to an ethynyl, cyano, or diazonium substituent capable of π overlap with the carborane vertex. This conclusion[10f] was based upon both experimental and computed bond lengths, and spectroscopic measurements involving UV, IR, and NMR analyses.

The stereoelectronic effects of exhaustive B-methylation upon these properties has not been previously investigated either through experimental or computational studies except for a detailed investigation of the effect of permethylation on the electronic properties of the [*closo*-1-CB_9H_{11}]$^{-}$[11a] and [*closo*-$B_{12}(CH_3)_{12}$]$^{2-}$[11b] ions. Due to the potential perturbation of ground-state electronic effects as a result of exhaustive B-methylation of *para*-carborarods, relevant structural studies with 12- and 10-vertex carborarod model species are reported here which compare B-permethylated model species with their B–H analogues. Four of the compounds employed in this study have been structurally characterized (**3**,[10f] **4**,[13] **40**,[10f] and **41**). An additional determination of the structure of **40** was previously carried out by us at 100 K and not reported at the time.[40] The structure of **40** reported by Kaszynski was determined at 173 K. Both structures are given equal weight in the discussion (Table 1 and Figure 5).

Table 1 reports pertinent experimental and computed bond lengths for 12- and 10-vertex model compounds **3**, **4**, **11**, **40**, **41**, **43**, **44**, and **45** with and without B-methylation and trimethylsilylation of the terminal ethynyl groups. Computations were carried out at the HF/6-31G* level of theory.[41]

The presence of π-electron donation from the carborane cage to ethynyl groups in the ground state is expected to be

Table 1. The computed and *experimentally observed* bond lengths [Å] for *para*-carborarod modules.[a]

Carborarod structure[b]	-C≡C-	-C_{cage}–C≡	$(CH_3)_3$Si–C≡
44 $(Me_3SiC{\equiv}C)_2$[Me10]	1.196	1.438	1.853
45 $(HC{\equiv}C)_2$[Me10]	1.187	1.439	
3 $(Me_3SiC{\equiv}C)_2$[10]	1.195	1.438	1.856
	1.199[c]	*1.436*[c]	*1.848*[c]
43 $(HC{\equiv}C)_2$[10]	1.185[d]	1.439[d]	
41 $(Me_3SiC{\equiv}C)_2$[Me12]	1.196	1.448	1.857
	1.203[e]	*1.446*[e]	*1.850*[e]
11 $(HC{\equiv}C)_2$[Me12]	1.185	1.450	
40 $(Me_3SiC{\equiv}C)_2$[12]	1.195	1.449	1.858
	1.193[f]	*1.452*[f]	*1.857*[f]
	1.201[e]	*1.450*[e]	*1.854*[e]
4 $(HC{\equiv}C)_2$[12]	1.187	1.450	
	1.180[g]	*1.451*[g]	
30 $(MeOOCC{\equiv}C[Me12]C{\equiv}C)_2$	*exo 1.189*[e]	*exo 1.440*[e]	

[a] Hartree–Fock/6-31G* level of theory. [b] [Me10], [Me12], [10], and [12] represent *closo*-1,10-$C_2B_8(CH_3)_8$-1,10-ylene, *closo*-1,12-$C_2B_{10}(CH_3)_{10}$-1,12-ylene, *closo*-1,10-$C_2B_8H_8$-1,10-ylene, and *closo*-1,12-$C_2B_{10}H_{10}$-1,12-ylene, respectively. [c] Ref. [10c]. [d] Identical values obtained in ref. [10f]. [e] This work. [f] Ref. [10f]. [g] Averaged value of two structures present in the crystal as reported in ref. [13].

manifested by an "allenic distortion"[10f] in which the cage carbon vertex to the ethynyl carbon single bond is shortened by increased bond order while the ethynyl carbon–carbon triple bond is lengthened. Perusal of the collected list of computed and observed bond lengths associated with this array of C atoms in the model compounds suggests a random distribution of bond lengths as the carborane cage size, the presence or absence of *B*-methyl substituents, and the use of trimethylsilylethynyl or ethynyl groups are varied. However, a graphical treatment of the computed C−C bond lengths provided correlations to which the experimental values could be favorably compared. These correlations are derived from simple plots of computed -C≡C- lengths versus the corresponding C_{cage}−C≡ lengths for all 12- and 10-vertex carborane derivatives. Two linear relationships were obtained (Figure 5): one for the 10-vertex carborane derivatives and the other for the correspondingly substituted 12-vertex species.

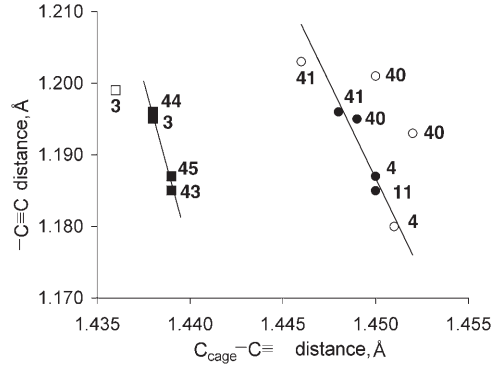


Figure 5. Plots of -C≡C- versus C_{cage}−C≡ employing computed and experimentally determined bond lengths for the carborarod model species listed in Table 1. Numerals are compound identification numbers. Least-squares treatment of the plots of computed bond lengths resulted in the two indicated linear relationships which differ in slope (10-vertex: $y = -9.500x + 14.856$, $r^2 = 0.973$ (left slope); 12-vertex: $y = -5.363x + 8.964$, $r^2 = 0.853$ (right slope)). Key: ● = C_2B_{10}, ■ = C_2B_8, ○ = C_2B_{10}-exptl, □ = C_2B_8-exptl.

Comparison of **44**/**3**, **45**/**43**, **41**/**40**, and **11**/**4** data-point pairs, which differ only by the presence or absence of B-permethylation, proves that B-permethylation does not affect computed ground-state bond lengths. However, the terminal trimethylsilylation of *C*-ethynyl groups appears to lengthen the computed -C≡C- distances relative to the unsubstituted analogues by about 0.01 Å in both the 10- and 12-vertex carborane derivatives. This could be the result of π donation from the alkyne linkage to empty silicon d or σ* orbitals. The slopes of the two correlation lines differ by a factor of 1.75 and both are in agreement with the "allenic distortion" expected of weak ground-state π-electron donation from the 10- and 12-vertex carborane cages into conjugated ethynyl groups with (**44**, **3**, **41**, and **40**) or without (**45**, **43**, **4**, and **11**) conjugation with silicon orbitals.

The marked separation of the 10- and 12-vertex correlation lines on the C_{cage}−C≡C axis (Figure 5) is not unexpected, as the hybridization of the apical carbon atoms of the 10- and 12-vertex cages differs with greater p character associated with the 12-vertex cage ($sp^{2.26}$ in **4** and $sp^{2.17}$ in **43** were indicated[10f] from NBO 3.1 calculations).[10f,42] Indeed, the comparison of C_{cage}−C substituent bond lengths for 10- and 12-vertex cage structures invariably demonstrates longer bonds for the 12-vertex cage even when the C-substituent is incapable of conjugation with the C_{cage} vertex. The experimental C_{cage}−$CH_2(CH_2)_5CH_3$ distances in 1,1′-bis[12-nC_7H_{15}-1,12-$C_2B_{10}H_{10}$] (**1**; 1.534 Å) and 1,1′-bis[10-nC_7H_{15}-1,10-$C_2B_8H_8$] (**2**; 1.513 Å) serve as examples.[10a] Similarly, the experimental 1,1′ intercage bond lengths in these two compounds are 1.546 and 1.461 Å, respectively.

The reasonably good agreement of the correlation lines based upon individual compounds with their experimentally determined values reinforces the reliability of the former data.

The dimeric carborarod derivative **30** displays bond lengths associated with the *exo*-C≡C- (1.189 Å) and *exo*-C_{cage}−C≡ (1.440 Å) that are in agreement with the lengths of the bond types found in other molecules reported here. As expected, a possible ground-state structural manifestation of B-permethylation could not be discerned.

Electronic spectra of 12-vertex model species (**4**, **11**, **40**, and **41**) displayed strong absorption at wavelengths shorter than 200 nm, but beyond the capability of solution measurements. Carborarods with one or more 1,4-butadiynylene components displayed only strong allowed absorptions attributable to that structural feature near 200 nm and above (**29**: λ ($\varepsilon \times 10^{-3}$) = 204 (91), 211 (138), 221 nm (132 $mol^{-1} dm^3 cm^{-1}$); **19**: λ ($\varepsilon \times 10^{-3}$) = 198 (87), 206 (104), 215 nm (85 $mol^{-1} dm^3 cm^{-1}$); (*t*BuC≡C-)$_2$: λ ($\varepsilon \times 10^{-3}$) = 177 (72), 185 (82), 215 nm (87 $mol^{-1} dm^3 cm^{-1}$)). Carborarod **26** with four permethylated 12-vertex carborane cages was not sufficiently soluble in hexane to provide UV data.

The B-permethylated *para*-carborane model species described here allowed the effects of B-permethylation on ^{13}C and ^{11}B chemical shifts to be examined in several structural environments derived from *p*-carborane. Other studies involving the methylation of polyhedral borane and carborane derivatives have been previously reported.[11] Taken together, these results prove that both C- and B-methylation result in deshielding of the methylated vertices and the effect of B-permethylation is unremarkable. The ^{11}B chemical shifts (δ) observed generally fall in the range of −16 to 0 ppm (for *closo*-$C_2B_{10}H_{12}$, ^{11}B NMR: $\delta = -15.0$ ppm). The methyl group is an electron-withdrawing group relative to the boron atom to which it is bonded because the electronegativities of B and C are approximately 2.0 and 2.5, respectively. Hydrogen, which is replaced by a methyl carbon atom, has an electronegativity of 2.2. Consequently, methyl is a −I substituent on boron with +M capability under sufficiently electron-demanding conditions.

Platinum(II)-linked B-permethylated carborarods: Transition metal fragments are widely employed as endcaps or junctions in *s*-acetylide complexes.[43] Extraordinarily long polyynes and macromolecular constructs, as well as hydrocarbon-soluble acetylenic polymers, have been synthesized, which exploit the electronic stabilization and well-defined geometries of transition-metal centers.[44] Consequently, the linkage of the selected alkyne-substituted *para*-carborarods described above with platinum centers was explored by using the $[(PR_3)_2Pt]^{2+}$ (R = Et, *n*Bu) moiety (Scheme 8). These reactions were performed in accordance with the procedure of Hagihara et al.[45]

Initially, *cis*-$[(n\mathrm{Bu}_3P)_2PtCl_2]$ was reacted with alkyne **17** in the presence of cuprous iodide and $HNEt_2$ to yield **46** with stereochemical rearrangement at the Pt center. Likewise, *trans*-$[(n\mathrm{Bu}_3P)_2PtCl_2]$ and dimeric *para*-alkyne **24** gave **47**. Single crystals of **47** which appeared to be suitable for an X-ray diffraction study were obtained, but unfortunately the structure could not be sufficiently refined to provide accurate bond lengths and angles. The resulting low-resolution structure is presented in Figure 6 and confirms the synthesis and general structure of the intended reaction product.

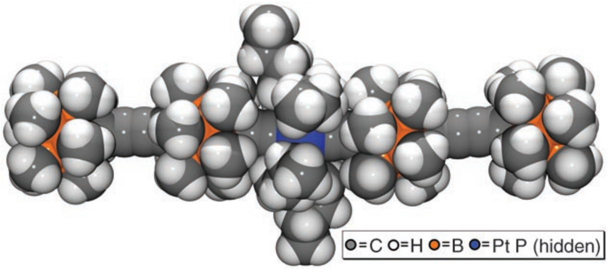
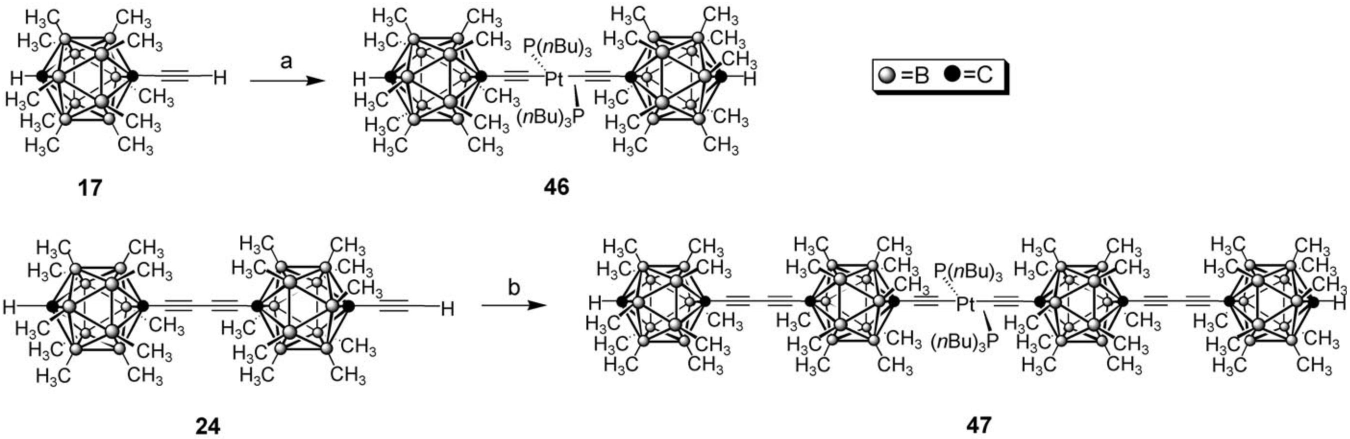
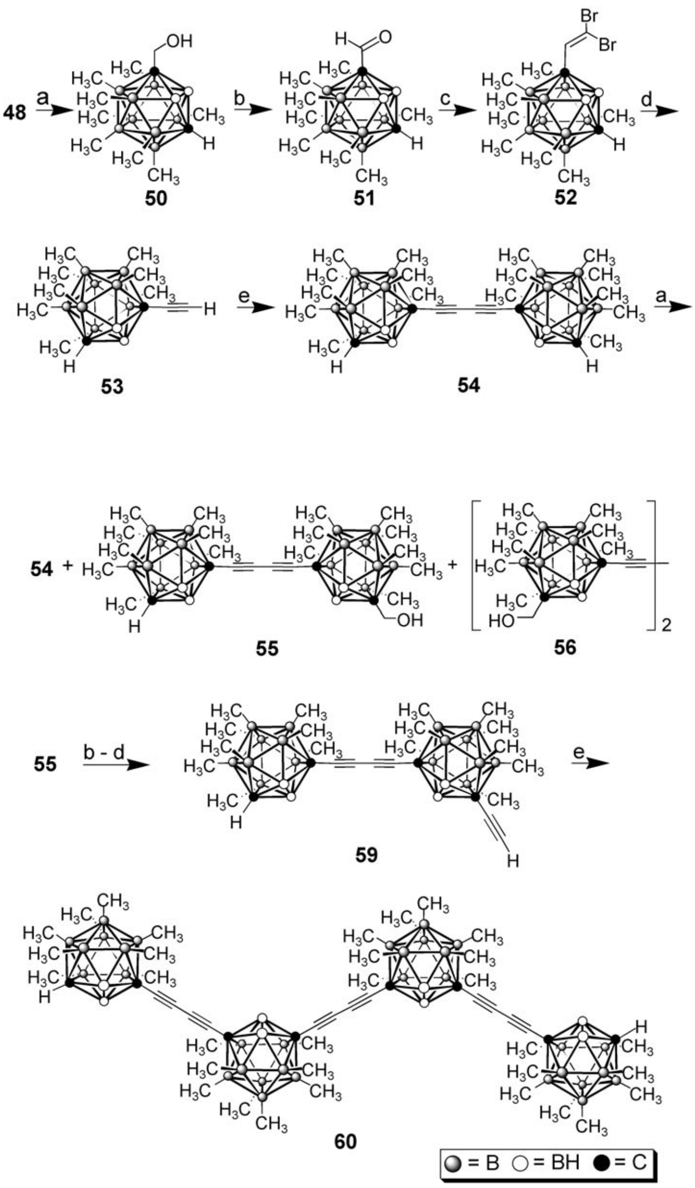


Figure 6. Space-filling representation of the structure of B-permethylated platina–carborarod **47**. The structure could not be further refined due to poor crystal quality.

Synthesis of highly B-methylated *m*-carborarods: The synthesis of the butadiynylene-linked rod analogues of **29** and **36** (Scheme 5) based on octamethyl-1,7-dicarbadodecaborane (**48**) appeared to be an attractive goal. In particular, it was important to determine whether the resulting zigzag 1,7-carborarod conformers would exhibit improved solubility in organic solvents compared with their linear 1,12-carborarod counterparts. As in the case of **6** (Scheme 1), the direct coupling of acetylene residues with **48** was unsuccessful and an alternative synthetic approach was required to generate the *C*-ethynyl moiety. In a pathway analogous to that employed for **6** (Scheme 1), the 1-(2-hydroxyethyl) derivative of **48** (i.e., **49**) was prepared in a high yield by using metalation with CH_3Li in THF followed by the addition of ethylene oxide. Protection of the second C−H vertex of **48** was not required, however. Swern oxidation of **49** generated a mixture of the corresponding aldehyde and its enol tautomer in solution (as judged by NMR measurements) and the chromatographic separation on silica gel may have failed due to hemiacetal formation between the enol and the aldehyde. Alternatively, the 1-hydroxymethyl derivative of **48** (i.e., **50**) was oxidized to carboxyaldehyde **51**. Aldehyde **51** was converted to the 1-(2,2-dibromovinyl) derivative **52**.[30] In contrast to **9** (Scheme 2), **51** reacted slowly with $Ph_3P{=}CBr_2$ (prepared in situ), and the highest yield of **52** was achieved by heating a mixture of PPh_3, CBr_4, and **51** in CH_2Cl_2 for 36 h.[46] The 1-ethynyl derivative **53** was obtained in an 78 % yield by reductive dehydrobromination of **52** with $NaNH_2$/liquid ammonia without the formation of the vinyl side product. This is to be contrasted with the dehydrochlorination of the 2,2-dichloroethylated *para*-carborane intermediate, which was accompanied by the formation of the undesirable vinyl compound. Coupling of **53** (Glaser) afforded the rigid dimeric rod **54** (Scheme 9). Employment of these transformations with **54** as the starting material furnished the tetrameric rod **60**, the *meta*-analogue of **26** (Scheme 4). As in the case of *para*-carborarod **26**, compound **60** is a colorless, thermally robust, microcrystalline solid which is sparingly soluble in hexanes, but dissolves well in hot aromatic solvents.



Scheme 8. Synthesis of platinum rod **47**. a) *cis*-$[Cl_2Pt(P\text{-}n\mathrm{Bu}_3)_2]$, CuI, Et_2NH, RT, 12–18 h; b) *trans*-$[Cl_2Pt(P\text{-}n\mathrm{Bu}_3)_2]$, CuI, Et_2NH, RT, 12–18 h.



Scheme 9. Synthesis of tetrameric *meta*-carborane rod **60**. a) CH_3Li $(CH_2O)_n$; b) $(COCl)_2$, DMSO, $i Pr_2NEt$; c) CBr_4, PPh_3; d) $NaNH_2$, NH_3; e) CuCl, O_2, py, DBU, 45 °C, 2 h. Product distribution **54**/**55**/**56** = 1:3:1.

Conclusion

Examination of computed and, where possible, experimental bond lengths associated with *C*,*C'*-diethynyl (and the corresponding $C{\equiv}C{-}Si(CH_3)_3$) derivatives of 10- and 12-vertex *para*-carboranes and their B-permethylated analogues has revealed no discernible effect of B-permethylation upon those bond lengths, as expected. Possible perturbations based upon electron-release through hyperconjugation of $B{-}CH_3$ groups have not materialized, undoubtedly due to the very small contribution of such interactions to ground-state structural properties. However, the $C_{cage}{-}C{\equiv}$ single-bond lengths observed in 10- and 12-vertex carborane derivatives differ by approximately 0.01 Å with the 10-vertex species having the shorter bonds (Figure 5). This relative shortening of the $C_{cage}{-}C{\equiv}$ bond has previously been associated[10f] with more effective $C_{cage}{-}C{\equiv}C$ π overlap of the carbon vertices of the 10-vertex cage compared with those of the 12-vertex counterpart. An alternative explanation based upon hybridization differences between the carbon vertices of the 10- and 12-vertex cages ($sp^{2.17}$ and $sp^{2.26}$, respectively[10f]) is preferred for the reasons described above. The different sensitivities of $C_{cage}{-}C{\equiv}$ bond lengths to changes in cage substitution (permethylation, ethinyl group trimethylsilylation) as the cage size is changed from 10- to 12-vertices (slopes of correlation lines; Figure 5) may be a further manifestation of cage-carbon hybridization differences. Differences in bond-length response of the two cage types as a result of substituent changes leading to differing slopes of the correlation lines is confined to changes in $C_{cage}{-}C{\equiv}$ bond lengths, the linkage most affected by C_{cage} hybridization differences.

The steric "bumper-car" effect resulting from B-permethylation of 12-vertex *para*-carborane and B-octamethylation of *meta*-carborane modules protects the 1,4-butadiynylene components of the corresponding carborarods from external attack and enhances their thermal stabilities. A manifestation of this phenomenon is the high temperatures (>350 °C) required for decomposition to occur. At the same time, the solubilities of the highly B-methylated species of all types are markedly increased above those of their unsubstituted counterparts.

As a result of this work it is evident that B-permethylation of *para*-carborane and B-octamethylation of *meta*-carborane cages may be utilized to stabilize carborarod derivatives suitable for use as components in "bottom-up" nanodevice design.

Experimental Section

General methods: Tetrahydrofuran (THF) and benzene were distilled from sodium metal. CH_2Cl_2, dimethylsulfoxide (DMSO), pyridine, triethylamine, and diisopropyldiethylamine (Hünig's base) were distilled from CaH_2 prior to use. Methyllithium, ethylene oxide, oxalyl chloride (99.8 %), methyl chloroformate, *n*-butyl chloroformate, methyl formate, PCl_5, PPh_3, CBr_4, CH_3MgBr, *n*BuLi, *t*BuOK, SO_3·Py, CuCl, and CuI were used as purchased (Aldrich). Oxygen was used as purchased (99.99 %, Mattheson). The reagents sodium amide in liquid ammonia,[27] *cis*- and *trans*-$[Cl_2Pt(P\text{-}nBu_3)_2]$,[47] *cis*-$[Cl_2Pt(PEt_3)_2]$,[47] $(Ph_3PCH_2Cl)Cl$[48] as well as the starting materials 1,12-bis(hydroxymethyl)-1,12-dicarbadodecaborane(12) (**37**),[49] 2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (**6**),[20d] and *closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaborane(12) (**48**)[20d] were prepared in accordance with literature methods. Reactions were performed under argon using Schlenk techniques. All NMR spectra were recorded with Bruker ARX 400 and 500 spectrometers. Infrared spectra were obtained with a Nicolet Nexus 470 using KBr pellets. UV data of solutions in hexane were collected on an Agilent 8453 spectrometer. Mass spectra were obtained by using a VG ZAB-SE (FAB) and a VG Autospec (EI) mass spectrometer. Elemental analyses were performed at the Department of Chemistry, University of Pennsylvania.

Computational methods: Both ab initio and NBO calculations were carried out on Linux Beowulf Cluster parallel computers using the Gaussian 98 package[41] at HF/6-31G* level.

1,12-Bis(2-hydroxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (7): Methyllithium (20.1 mL, 28.1 mmol, 1.4 M in Et_2O) was added to a solution of **6** (2.00 g, 7.00 mmol) in THF (150 mL) at 0 °C, warmed to 40 °C, and stirred for 3 h. Upon cooling again to 0 °C, ethylene oxide (1.50 mL, 30.0 mmol) was added by using a precooled syringe. After the mixture had been stirred for 2 h at ambient temperature, all volatiles were removed under reduced pressure. Aqueous 10% HCl (10 mL) and Et_2O were added to the residue and the suspension was filtered (Büchner funnel). The residue was washed with water and Et_2O and dried in vacuo to yield **7** as a colorless solid (1.68 g, 65%). M.p. >350 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.45$ (t, $J = 8.5$ Hz, 4H; CH_2OH), 1.67 (t, $J = 8.4$ Hz, 4H; CH_2CH_2OH), 1.45 (br s; OH), 0.03 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 75.3$ (br s; carboranyl C), 59.6 (s; CH_2OH), 34.8 (s; CH_2CH_2OH), −3.0 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.4$ ppm (s); HRMS (EI): m/z: calcd: 372.4040; found: 372.4021 [M^+].

1,12-Bis(vinyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (8): A mixture of **7** (2.44 g, 6.55 mmol) and $Al(OiPr)_3$ (2.81 g, 13.8 mmol) in toluene was heated under reflux for 2.5 h. The solvents and *i*PrOH were distilled off and the residue was heated at 300 °C for 1 h. Dilute HCl was added and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried under reduced pressure and the residue was purified by using flash chromatography on silica gel using first pentane and then Et_2O. The Et_2O fraction contained unreacted **7** whereas removal of the pentane in vacuo gave **8** as a colorless solid (1.87 g, 85%). M.p. 250 °C (subl.); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.15$–5.10 (m, 4H; CH_2CH), 4.80 (dd, $J_{trans} = 14.5$, $J_{cis} = 4.4$ Hz, 2H; CH_2CH), 0.00 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 130.6$ (s; CH_2CH), 120.5 (s; CH_2CH), 81.5 (br s; carboranyl C), −4.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -8.7$ ppm (s; BCH_3); HRMS (EI): m/z: calcd: 336.3825; found: 336.3828 [M^+].

1,12-Bis(2-oxoethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (9): To a solution of **7** (1.50 g, 4.00 mmol) in CH_2Cl_2 (10 mL), DMSO (5 mL), and Et_3N (6.70 mL, 48.0 mmol), a solution of sulfur trioxide–pyridine complex (3.85 g, 24.0 mmol) in DMSO (10 mL) was added. The reaction mixture was stirred at ambient temperature for 2.5 h and then partitioned between aqueous $NaHCO_3$ solution (3%) and Et_2O. The aqueous phase was extracted with Et_2O (3 × 20 mL) and the combined ethereal extracts were washed with water and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by using flash chromatography on a short bed of silica gel with Et_2O/petroleum ether (1:1). The dried eluant consisted of pure colorless **9** (1.10 g, 75%). M.p. >355 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 9.45$ (t, $J = 3.3$ Hz, 2H; CHO), 2.33 (d, $J = 3.3$ Hz, 4H; CH_2), 0.07 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 197.6$ (s; CHO), 74.8 (br s; carboranyl C), 44.9 (s; CH_2), −3.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.8$ ppm (s); IR (KBr): $\tilde{\nu} = 2948$, 2910, 2835, 1723 (C=O), 1685, 1324, 1152, 1056, 920 cm^{-1}; HRMS (EI): m/z: calcd: 368.3727; found: 368.3708 [M^+].

1,12-Bis(2,2-dichloroethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (10): To a solution of **9** (1.10 g, 3.00 mmol) in benzene, PCl_5 (2.50 g, 12.0 mmol) was added. The reaction mixture was stirred for 5 h, quenched with cold aqueous $NaHCO_3$ solution, and the aqueous layer was extracted with petroleum ether (6 × 30 mL). The combined organic phases were dried over $MgSO_4$ and were purified by using flash chromatography on a short bed of silica gel. Removal of the solvent furnished colorless **10** (1.08 g, 75%). M.p. 250 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.57$ (t, $J = 4.3$ Hz, 2H; $CHCl_2$), 2.58 (d, $J = 4.3$ Hz, 4H; CH_2), 0.11 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 77.3$ (s; carboranyl C), 69.2 (s; $CHCl_2$), 48.3 (s; CH_2), −3.6 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.8$ ppm (s); IR (KBr): $\tilde{\nu} = 2948$, 2910, 1429, 1327, 1152, 950, 931, 705 cm^{-1}; HRMS (EI): m/z: calcd: 478.2550; found: 478.2549 [M^+].

1,12-Bis(*n*-butyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (12): To a freshly prepared suspension of $NaNH_2$ (0.650 g, 16.8 mmol) in liquid NH_3 (30 mL), a solution of **11** (1.00 g, 2.10 mmol) in Et_2O (60 mL) was added through a cannula. The reaction mixture was allowed to warm to ambient temperature and was quenched with dilute aqueous HCl. The aqueous phase was extracted with hexanes (6 × 30 mL) and the combined organic extracts were dried over $MgSO_4$ and filtered. The solid obtained after removal of solvent was dissolved in anhydrous THF (50 mL) and a solution of methyllithium (3.75 mL, 5.30 mmol, 1.4 M in Et_2O) was added at 0 °C. The reaction mixture was stirred for 0.5 h at ambient temperature, was cooled to −78 °C, and *n*-butyl chloroformate (0.76 g, 6.00 mmol) was added. The reaction mixture was allowed to warm to ambient temperature, was stirred for 5 h, and then quenched with aqueous $NaHCO_3$ solution. The aqueous layer was extracted with petroleum ether (3 × 30 mL) and the combined organic phases were dried over $MgSO_4$. All volatiles were removed under reduced pressure and the residue was purified by using chromatography on silica gel (Et_2O/petroleum ether 1:10) to afford **12** as a colorless solid (0.84 g, 75%). M.p. 103 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 4.13$ (t, $J = 6.7$ Hz, 4H; OCH_2), 1.62 (tt, $J = 6.7$ Hz, 4H; CH_2), 1.35 (tt, $J = 6.7$ Hz, 4H; CH_2), 0.92 (t, $J = 6.7$ Hz, 6H; CH_2CH_3), 0.10 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 153.1$ (s; COO), 80.0 (s; $C{\equiv}CCOO$), 77.8 (s; $CCOO$), 73.9 (br s; carboranyl C), 66.4 (s; OCH_2), 30.5, 19.2 (2s; CH_2), 13.8 (s; CH_2CH_3), −4.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.8$ ppm (s); HRMS (EI): m/z: calcd: 532.4569; found: 532.4562 [M^+].

1,12-Bis(ethynyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (11): A mixture of diester **12** (0.800 g, 1.50 mmol) and LiI (0.80 g, 6.00 mmol) was heated at reflux in anhydrous 2,6-lutidine (25 mL) for 3 h. The lutidine was removed in vacuo and the residue was quenched with 10% aqueous HCl. The water phase was extracted with hexanes (6 × 30 mL) and the combined organic extracts were dried over $MgSO_4$, filtered through a short bed of silica gel, and dried under reduced pressure to yield **11** as a colorless solid (0.49 g, 98%). M.p. >355 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.46$ (s, 2H; CH), 0.06 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 76.7$ (s; $C{\equiv}CH$), 75.4 (s; $\equiv CH$), 74.4 (br s; carboranyl C), −4.1 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.8$ ppm (s); UV/Vis (*n*-hexane): $\lambda = < 200$ nm; HRMS (EI): m/z: calcd: 332.3515; found: 332.3521 [M^+].

1-(2-Hydroxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (13): Methyllithium (12.6 mL, 17.6 mmol, 1.4 M in Et_2O) was added to a solution of **6** (5.00 g, 17.6 mmol) in THF (150 mL) at 0 °C. The solution was allowed to warm to ambient temperature and was stirred for an additional 8 h. At 0 °C, ethylene oxide (1.00 mL, 20.0 mmol) was added by using a precooled syringe. After the mixture was slowly allowed to warm to ambient temperature (2 h), all volatiles were removed under reduced pressure. Aqueous 10% HCl (30 mL) was added to the residue and the aqueous phase was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the Et_2O was removed under reduced pressure. The residue was purified by using chromatography on silica gel (Et_2O/pentane 1:3) yielding **13** as a colorless solid (5.43 g, 94%, $R_f = 0.55$). M.p. 355 °C (decomp); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.43$ (t, $J = 8.4$ Hz, 2H; CH_2OH), 2.02 (s, 1H; carboranyl CH), 1.67 (t, $J = 8.4$ Hz, 2H; CH_2CH_2OH), 1.42 (br s, 1H; OH), 0.04 (s, 15H; BCH_3), 0.03 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 77.3$ (br s; carboranyl C), 75.1 (br s; carboranyl C), 59.7 (s; CH_2OH), 34.7 (s; CH_2CH_2OH), −3.0 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -7.1$ (s, 5B), −8.5 ppm (s, 5B); HRMS (EI): m/z: calcd: 328.3769; found: 328.3772 [M^+].

1-Vinyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (14): A mixture of **13** (1.00 g, 3.00 mmol) and $Al(OiPr)_3$ (6.10 g, 30.0 mmol) in toluene (35 mL) was heated under reflux for 0.5 h. The volatiles were distilled off and the residue was heated at 300 °C for 1 h. Dilute HCl was added and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried under reduced pressure and the residue was purified by using flash chromatography on silica gel using first pentane and then Et_2O. The Et_2O fraction contained unreacted **13** whereas removal of the pentane in vacuo gave **14** as a colorless solid (576 mg, 61%). M.p. 296 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.14$–5.04 (m, 2H; CH_2CH), 4.78–4.73 (m, 1H; CH_2CH), 2.09 (s, H; carboranyl CH), 0.06 (s, 15H; BCH_3), 0.01 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 130.3$ (s; CH_2CH), 120.4 (s;

CH_2CH), 79.6 (brs; carboranyl C), 75.9 (brs; carboranyl C), −3.5 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.9$ (s, 5B), −8.4 ppm (s, 5B); HRMS (EI): m/z: calcd: 310.3664; found: 310.3670 [M^+].

1-(2-Oxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (15): Neat DMSO (3.30 mL, 46.5 mmol) was slowly added dropwise to a solution of oxalyl chloride (2.00 mL, 23.3 mmol) in CH_2Cl_2 (200 mL) at −62 °C. After gas evolution had ceased, anhydrous **13** (5.10 g, 15.5 mmol) was added. The reaction mixture was allowed to warm to 30 °C (1 h), was cooled to −78 °C, and then NEt_3 (7.56 mL, 54.2 mmol) was added. After the reaction mixture had warmed to ambient temperature, all volatile components were removed under vacuum and the remaining residue was quenched with water (50 mL). The water layer was extracted twice with pentane (2×50 mL). The pentane was distilled off under reduced pressure and the resulting solid was purified by using flash chromatography on silica gel with Et_2O/pentane (1:10). Removal of the solvent in vacuo afforded **15** (4.96 g, 98 %). M.p. 322 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=9.45$ (t, $J=3.3$ Hz, 1H; CHO), 2.32 (d, $J=3.6$ Hz, 2H; CH_2), 2.11 (s, 1H; carboranyl CH), 0.07 (s, 15H; BCH_3), 0.05 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=$ 198.1 (s; CHO), 75.5 (s; carboranyl C), 73.9 (s; carboranyl C), 45.0 (s; CH_2), −3.7 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-5.5$ (s, 5B), −6.7 ppm (s, 5B); HRMS (EI): m/z: calcd: 326.3613; found: 326.3602 [M^+].

1-(2,2-Dichloroethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (16): Phosphorus pentachloride (9.20 g, 44.1 mmol) was added to a solution of **15** (4.80 g, 14.7 mmol) in benzene (100 mL) at 0 °C. The suspension was stirred for 8 h at ambient temperature and hydrolyzed by ice water. The aqueous layer was extracted twice with pentane (50 mL). The pentane was distilled off under reduced pressure and the obtained solid was purified by using flash chromatography on silica gel with pentane. Removal of the solvent in vacuo afforded **16** (4.76 g, 85 %). M.p. 242 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=5.59$ (t, $J=$ 4.0 Hz, 2H; $CHCl_2$), 2.59 (d, $J=4.0$ Hz, 2H; CH_2), 2.10 (s, 1H; carboranyl CH), 0.11 (s, 15H; BCH_3), 0.01 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=76.3$ (s; carboranyl C), 75.9 (s; carboranyl C), 69.5 (s; $CHCl_2$), 48.3 (s; CH_2), −3.6 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-5.6$ (s, 5B), −6.7 ppm (s, 5B); HRMS (EI): m/z: calcd: 381.3004; found: 381.3006 [M^+].

1-Ethynyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (17) and 1-(methyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (18): To a suspension of sodium amide (59.0 mmol) in anhydrous ammonia (150 mL)—prepared from sodium metal (1.36 g, 59.0 mmol) and $FeCl_3{\cdot}6H_2O$ (2.00 mg, 0.07 mmol)—a solution of dichloride **16** (4.50 g, 11.8 mmol) dissolved in Et_2O (50 mL) was added through a cannula. The ammonia was allowed to evaporate and the remaining suspension was hydrolyzed at 0 °C with a saturated aqueous NH_4Cl solution. The off-white solid obtained, after extraction of the water layer with pentane (3×50 mL) and evaporation of the solvent, was purified by using flash chromatography on silica gel with pentane. Removal of the solvent in vacuo afforded a mixture of **17** (91 %) and **14** (3 %) (3.42 g total weight). The mixture was redissolved in anhydrous Et_2O (200 mL) and *t*BuLi (8.82 mL, 15 mmol, 1.7 M in pentane) was added dropwise at −78 °C. At −18 °C, methyl chloroformate (1.84 g, 1.51 mL, 19.5 mmol) was added. Extraction with pentane, removal of the solvent, and chromatography of the resulting solid residue on a short bed of silica gel (Et_2O/pentane 1:15) provided **14** (108 mg, $R_f=0.9$) and **18** (3.86 g, 10.5 mmol, $R_f=0.6$). Ester **18** was heated under reflux in 2,6-lutidine (50 mL) in the presence of LiI (2.80 g, 21.0 mmol) for 6 h. The lutidine was distilled off and the residue was quenched with aqueous 10 % HCl (25 mL). The solid obtained upon extraction with pentane and removal of the solvent was purified by using flash chromatography on silica gel (pentane). The dried filtrate contained pure **17** (3.20 g, 88 % relative to **16**). **17**: M.p. 342 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=2.41$ (s, 1H; CH), 2.08 (s, 1H; carboranyl CH), 0.09 (s, 15H; BCH_3), 0.03 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=76.3$ (s; carboranyl C), 76.1 (s; carboranyl C), 75.2 (s; $C{\equiv}CH$), 73.1 (s; $C{\equiv}CH$), −3.7 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, pentane): $\delta=-4.9$ (s, 5B), −7.3 ppm (s, 5B); HRMS (EI): m/z: calcd: 308.3507; found: 308.3508 [M^+]. **18**: M.p. 279 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=3.63$ (s, 3H; $COOCH_3$), 2.06 (s, 1H; CH), 0.00 (s, 15H; BCH_3), −0.04 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=153.6$ (s; COO), 78.7 (s; $C{\equiv}CCOO$), 78.5 (s; $C{\equiv}CCOO$, overlapping with $CDCl_3$ signal), 73.5 (s; carboranyl C), 71.2 (s; carboranyl C), 53.0 (s; $COOCH_3$), −4.1 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.2$ (s, 5B), −8.5 ppm (s, 5B); HRMS (EI): m/z: calcd: 366.3562; found: 366.3555 [M^+].

1,1′-{Bis[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]}-1,4-butadiyne (19): Compound **17** (3.10 g, 10.0 mmol) and CuCl (50.0 mg, 0.0500 mmol) were dissolved in anhydrous pyridine (150 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.200 mL, 0.130 mmol) was added and oxygen was passed through the solution for 3 h at 45 °C by using a gas frit. All volatiles were removed in vacuo and after addition of aqueous 10 % HCl (50 mL) the product was extracted with benzene. The benzene was distilled off and the remaining residue was purified by using flash chromatography on silica gel with pentane. Removal of the solvent in vacuo afforded **19** (2.95 g, 96 %). M.p. >375 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=2.06$ (s, 2H; carboranyl CH), 0.07 (s, 30H; BCH_3), 0.00 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=$ 76.5 (brs; carboranyl C), 73.5 (brs; carboranyl C), 71.9 (s; CC), 71.3 (s; CC), −3.8 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, *n*-pentane): $\delta=$ −4.6 (s, 10B), −7.2 ppm (s, 10B); UV/Vis (*n*-hexane): λ_{max} ($\log\varepsilon$) = 198 (4.94), 206 (5.02), 215 (4.93), 243 (2.62), 256 (2.78), 270 nm (2.52); HRMS (EI): m/z: calcd: 615.6822; found: 615.6808 [M^+].

1-[12-(2-Hydroxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiyne (20) and 1,1′-bis[12-(2-hydroxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne (21): Methyllithium (3.40 mL, 4.40 mmol, 1.3 M in Et_2O) was added to a solution of **19** (2.70 g, 4.40 mmol) in THF (80 mL) at −30 °C. The solution was allowed to warm to ambient temperature and was stirred for an additional hour. The mixture was cooled to 0 °C and ethylene oxide (0.280 mL, 5.50 mmol) was added by using a precooled syringe. The reaction mixture was stirred for 2 h while slowly warming it to ambient temperature. All volatiles were removed under reduced pressure and aqueous HCl (30 mL) was added to the resulting residue. The aqueous layer was extracted with Et_2O (5×50 mL). The organic layers were combined and the Et_2O was removed under reduced pressure. The residue was washed onto a short bed of silica gel and washed thoroughly with hexanes. The dried filtrate contained unreacted **19** (541 mg, 20 %). The remaining mixture was removed from the column by using ethyl acetate as the eluent. The volume of the eluant was reduced to 20 mL. Precipitated material was filtered off and the filtrate was purified by means of chromatography (silica gel, ethyl acetate/hexanes 1:3) yielding **20** as a colorless solid (1.74 g, 60 %, $R_f=0.55$). The crystals as well as the late fraction ($R_f=0.35$) from the column are compound **21** (619 mg, 20 %). **20**: M.p. >375 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=$ 3.44 (t, $J=8.6$ Hz, 2H; CH_2OH), 2.06 (s, 1H; carboranyl CH), 1.69 (t, $J=$ 8.5 Hz, 2H; CH_2CH_2OH), 0.07 (s, 15H; BCH_3), 0.06 (s, 15H; BCH_3), −0.01 (s, 15H; BCH_3), −0.02 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=78.9$ (brs; carboranyl C), 76.5 (brs; carboranyl C), 73.4 (brs; carboranyl C), 72.9 (brs; carboranyl C), 72.0 (s; CC), 71.9 (s; CC), 71.6 (s; CC), 71.2 (s; CC), 59.6 (s; CH_2OH), 35.1 (s; CH_2CH_2OH), −3.9 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.5$ (s, 10B), −7.5 (s, 5B), −9.1 ppm (s, 5B); HRMS (EI): m/z: calcd: 658.7133; found: 658.7126 [M^+].

Compound **21** was obtained in 97 % yield by reacting **19** (1 molar equiv) with methyllithium (2.2 molar equiv) and quenching the mixture with ethylene oxide (2.5 molar equiv). Ethyl acetate was used for the extraction and the recrystallization. **21**: M.p. >375 °C; ^1H NMR (400.13 MHz, 325 K, $CDCl_3$): $\delta=3.46$ (t, $J=7.8$ Hz, 4H; CH_2OH), 1.71 (t, $J=8.0$ Hz, 4H; CH_2CH_2OH), 1.30 (s, 2H; OH), 0.07 (s, 30H; BCH_3), 0.01 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=90.0$ (brs; carboranyl C), 79.2 (brs; carboranyl C), 72.4 (s; CC), 71.7 (s; CC), 59.6 (s; CH_2OH), 35.3 (s; CH_2CH_2OH), −4.1 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.7$ (s, 10B), −7.8 ppm (s, 10B); HRMS (EI): m/z: calcd: 703.7372; found: 703.7361 [M^+].

1-[12-(2-Oxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiyne (22): As described above, the oxidation reagent was prepared from DMSO (0.520 mL, 7.30 mmol) and oxalyl chloride (0.320 mL, 3.60 mmol) in CH_2Cl_2 (80 mL) at −62 °C. To this mixture, a solution of anhydrous **20** (1.60 g, 2.40 mmol) in Et_2O was added through a cannula. The reaction mixture was allowed to warm to −30 °C over a period of 3 h, was cooled to −78 °C, and then NEt_3 (1.20 mL, 3.50 mmol) was added. Workup was conducted as described for the synthesis of **15** to afford **22** (1.52 g, 95 %). M.p. 370 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 9.44$ (t, $J = 3.2$ Hz, 1H; CHO), 2.33 (d, $J = 3.3$ Hz, 2H; CH_2), 2.07 (s, 1H; carboranyl CH), 0.08 (s, 15H; BCH_3), 0.07 (s, 15H; BCH_3), 0.02 (s, 15H; BCH_3), 0.00 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 197.9$ (s; CHO), 76.6 (br s; carboranyl C), 75.7 (br s; carboranyl C), 74.6 (br s; carboranyl C), 73.4 (br s; carboranyl C), 72.5 (s; CC), 72.1 (s; CC), 71.5 (s; CC), 71.0 (s; CC), 45.4 (s; CH_2), −3.9 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -6.1$ (s, 10B), −7.4 (s, 5B), −8.8 ppm (s, 5B); HRMS (EI): *m/z*: calcd: 656.6964; found: 656.6971 [M^+].

1-[12-(2,2-Dichloroethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiyne (23): A mixture of PCl_5 (1.30 g, 6.20 mmol) and **22** (1.40 g, 2.10 mmol) in benzene (30 mL) was reacted and the product isolated as described for the synthesis of **16** to afford **23** (1.30 g, 86 %). M.p. 282 °C; ^1H NMR (400.13 MHz, C_6D_6): $\delta = 5.48$ (t, $J = 4.0$ Hz, 2H; $CHCl_2$), 2.50 (d, $J = 4.0$ Hz, 2H; CH_2CHCl_2), 1.37 (s, 1H; carboranyl CH), 0.13 (s, 15H; BCH_3), 0.04 (s, 15H; BCH_3), 0.00 (s, 15H; BCH_3), −0.01 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 78.7$ (br s; carboranyl C), 76.8 (br s; carboranyl C), 75.0 (br s; carboranyl C), 73.8 (br s; carboranyl C), 73.6 (s; CC), 72.7 (s; CC), 72.6 (s; CC), 71.5 (s; CC), 69.7 (s; $CHCl_2$), 49.1 (s; CH_2), −3.8 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -6.1$ (s, 10B), −7.4 (s, 5B), −8.8 ppm (s, 5B); HRMS (EI): *m/z*: calcd: 711.6390; found: 711.6404 [M^+].

1-[12-Ethynyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiyne (24) and 1-[12-(methyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiyne (25): Dichloride **23** (1.20 g, 1.70 mmol) dissolved in Et_2O (50 mL) was cannulated into a freshly prepared suspension of $NaNH_2$ (330 mg, 8.50 mmol) in liquid ammonia (60 mL). Workup and purification were conducted as described in the first part of the synthesis of **17** to afford crude **24** (1.00 g, 96 %). Purification of **24** was carried out following the protection/deprotection procedure described for **17**. **24**: M.p. 322 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.47$ (s, 1H; CH), 2.09 (s, 1H; carboranyl CH), 0.11 (s, 15H; BCH_3), 0.08 (s, 15H; BCH_3), 0.06 (s, 15H; BCH_3), 0.03 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 77.0$ (s; $C{\equiv}CH$), 76.7 (s; carboranyl C), 75.4 (s; $\equiv CH$), 74.9 (br s; carboranyl C), 74.7 (br s; carboranyl C), 73.5 (br s; carboranyl C), 72.4 (s; CC), 72.1 (s; CC), 71.9 (s; CC), 71.1 (s; CC), −4.1 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, *n*-pentane): $\delta = -6.6$ (br s, 15B), −8.8 ppm (s, 5B); UV/Vis (*n*-hexane): λ_{max} ($\log\varepsilon$) = 209 (5.04), 218 (5.04), 243 (2.62), 257 (2.65), 272 nm (2.43); HRMS (EI): *m/z*: calcd: 639.6845; found: 639.6836 [M^+]. **25**: M.p. 285 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.72$ (s, 3H; OCH_3), 2.07 (s, 1H; carboranyl CH), 0.08 (s, 30H; BCH_3), 0.05 (s, 15H; BCH_3), −0.00 ppm (s, 15H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 153.3$ (s; COO), 79.3 (s; $C{\equiv}CCOO$), 78.5 (s; $C{\equiv}CCOO$), 76.7 (s; carboranyl C), 76.2 (br s; carboranyl C), 73.3 (br s; carboranyl C), 72.8 (s; CC), 72.6 (br s; carboranyl C), 72.4 (s; CC), 71.5 (s; CC), 70.8 (s; CC), 66.1 (s; COO), −4.1 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, pentane): $\delta = -6.6$ (br s, 15B), −8.8 ppm (s, 5B); HRMS (EI): *m/z*: calcd: 697.08; found: 697.08 [M^+].

12,12′-{Bis{1-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1,4-butadiynediyl}}-{1,1′-{bis[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne} (26): A mixture of **24** (0.900 g, 1.4 mmol), CuCl (1.00 mg, 0.10 mmol), and DBU (0.100 mL, 0.600 mmol) in anhydrous pyridine (25 mL) was reacted according to the procedure described for the synthesis of **19**. The product was extracted with hot toluene. The toluene was distilled off and the remaining residue was purified by using flash chromatography on a short bed of silica gel with toluene. Removal of the solvent afforded **26** which was washed with pentane and dried in vacuo (845 mg, 94 %). M.p. >355 °C; ^1H NMR (400.13 MHz, 100 °C, $[D_8]$toluene): $\delta = 1.55$ (s, 2H; carboranyl CH), 0.02 (br s, 90H; BCH_3), −0.01 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, 100 °C, $[D_8]$toluene): $\delta = 77.5$ (br s; 2× carboranyl C), 76.2 (br s; carboranyl C), 75.9 (br s; carboranyl C), 74.3 (s; CC), 74.2 (s; CC), 73.6 (s; CC), 73.2 (s; CC), 72.8 (s; CC), 72.0 (s; CC), −3.8 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, C_6D_6): $\delta = -7.4$ (br s, 30B), −10.1 ppm (s, 10B); elemental analysis calcd for $C_{60}H_{122}B_{40}$: C 56.47, H 9.63; found: C 55.96, H 9.87.

1,1′-{Bis[12-(2-oxyethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (27): To the oxidation reagent—prepared from DMSO (0.720 mL, 10.2 mmol), oxalyl chloride (0.500 mL, 5.70 mmol) in CH_2Cl_2 (350 mL) at −62 °C—anhydrous **21** (2.00 g, 2.80 mmol) was added. The reaction mixture was allowed to warm to −25 °C and was stirred for 5 h. At −78 °C, iPr_2NEt (2.20 mL, 12.8 mmol) was added. The workup of the reaction mixture was similar to that described for the preparation of **15** and **22**, to provide **27** (1.79 g, 90 %). M.p. 322 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 9.44$ (t, $J = 3.0$ Hz, 2H; CHO), 2.33 (d, $J = 2.8$ Hz, 4H; CH_2CHO), 0.07 (s, 30H; BCH_3), 0.02 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 197.8$ (s; CHO), 75.8 (br s; carboranyl C), 74.3 (br s; carboranyl C), 72.0 (s; CC), 71.8 (s; CC), 45.4 (s; CH_2), −4.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -6.1$ (s, 10B), −7.3 ppm (s, 10B); HRMS (EI): *m/z*: calcd: 699.7058; found: 699.7033 [M^+].

1,1′-{Bis[12-(2,2-dichloroethyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (28): Compound **27** (1.60 g, 2.30 mmol) and PCl_5 (3.00 g, 14.4 mmol) were reacted and the product was isolated according to the procedures used for the syntheses of **16** and **23**, affording **28** as a colorless solid (1.57 g, 85 %). M.p. 267 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.56$ (t, $J = 4.2$ Hz, 2H; $CHCl_2$), 2.59 (d, $J = 4.2$ Hz, 4H; CH_2), 0.13 (s, 30H; BCH_3), 0.00 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 78.1$ (br s; carboranyl C), 74.5 (br s; carboranyl C), 72.1 (s; CC), 71.9 (s; CC), 69.2 (s; $CHCl_2$), 48.6 (s; CH_2), −4.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -6.0$ (s, 10B), −7.4 ppm (s, 10B); HRMS (EI): *m/z*: calcd: 808.5909; found: 808.5904 [M^+].

1,1′-{Bis[12-ethynyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (29) and 1,1′-{bis[12-(methyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (30): Anhydrous tetrachloride **28** (1.45 g, 1.80 mmol), dissolved in Et_2O (30 mL), was cannulated into a freshly prepared suspension of $NaNH_2$ in liquid ammonia (50 mL), prepared from sodium (370 mg, 16.1 mmol) and $FeCl_3{\cdot}6H_2O$ (13.0 mg, 0.0500 mmol). Crude **29** (902 mg, 76 %) was isolated, converted to **30**, and **30** was purified and deprotected as described for compounds **17** and **24** to provide pure **29** as a colorless solid (860 mg, 72 %). **29**: M.p. >360 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.47$ (s, 2H; CH), 0.06 (s, 30H; BCH_3), 0.05 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 77.0$ (s; $C{\equiv}CH$), 75.4 (s; $\equiv CH$), 74.7 (br s; 2× carboranyl C), 72.5 (s; CC), 71.6 (s; CC), −4.2 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -6.8$ ppm (br s, 20B); UV/Vis (*n*-hexane): λ_{max} ($\log\varepsilon$) = 204 (4.96), 211 (5.14), 221 (5.12), 242 (2.93), 258 (2.82), 272 nm (2.44); HRMS (EI): *m/z*: calcd: 663.6846; found: 663.6851 [M^+]. **30**: M.p. 332 °C; ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.73$ (s, 6H; OCH_3), 0.08 (s, 30H; BCH_3), 0.04 ppm (s, 30H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 153.4$ (s; COO), 79.2 (s; $C{\equiv}COOCH_3$), 78.5 (s; $\equiv CCOOCH_3$), 75.9 (br s; carboranyl C), 72.8 (br s; carboranyl C), 72.4 (s; CC), 72.0 (s; CC), 53.1 (s; OCH_3), −4.0 ppm (br; BCH_3); $^{11}B\{^1H\}$ NMR (160.46 MHz, Et_2O): $\delta = -8.2$ ppm (br s, 20B); IR (KBr): $\tilde{\nu} = 2953$, 2909, 2835, 2243, 1726, 1435, 1323, 1287, 1202, 1171, 934, 748 cm^{-1}; HRMS (EI): *m/z*: calcd: 779.6959; found: 779.6892 [M^+].

1,1′-{Bis[12-(trimethylsilylethynyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (32): Methyllithium (2.00 mL, 2.80 mmol, 1.4 M in Et_2O) was added to a solution of **29**

(850 mg, 1.28 mmol) in THF (20 mL) at 0 °C. After 30 min, chlorotrimethylsilane (0.420 mL, 3.30 mmol) was added and stirring was continued for 3 h at ambient temperature. The solvents were removed under reduced pressure and water was added to the remaining off-white solid. Extraction of the water layer with pentane (3×50 mL) followed by passing the solution through a bed of silica gel and removal of the solvent in vacuo afforded **32** (1.00 g, 98 %). M.p. 321 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=0.11$ (s, 18 H; $SiCH_3$), 0.02 (s, 30 H; BCH_3), 0.01 ppm (s, 30 H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=96.4$ (s; ≡CSi), 94.8 (s; *C*≡CSi), 76.3 (br s; carboranyl C), 74.3 (br s; carboranyl C), 72.5 (s; CC), 71.5 (s; CC), 0.2 (s; $SiCH_3$), −4.3 ppm (br; BCH_3); ^{29}Si NMR (99.4 MHz, $CDCl_3$): $\delta=-16.9$ ppm (s); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.9$ ppm (br s, 20 B); UV/Vis (*n*-hexane): λ_{max} ($\log\varepsilon$) = 213 (4.89), 224 nm (4.91); HRMS (EI): *m*/*z*: calcd: 807.7645; found: 807.7635 [M^{+}].

1-[12-(Trimethylsilylethynyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[12′-(*n*-butyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne (33) and 1,1′-{bis[12-(*n*-butyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]}-1,4-butadiyne (31): The $CH_3Li{\cdot}LiBr$ complex (0.420 mL, 0.610 mmol, 1.45 M in Et_2O) was added dropwise to a solution of **32** (950 mg, 1.20 mmol) in THF (100 mL) at ambient temperature. The reaction mixture was stirred for an additional hour at ambient temperature and subsequently cannulated in small portions into a solution of *n*-butyl chloroformate (0.770 mL, 5.90 mmol) in THF (25 mL) at 0 °C. The reaction mixture was stirred for 3 h at ambient temperature. All volatile components were removed in vacuo, water was added to the remaining off-white solid, and the products were extracted with pentane (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. Chromatography (silica gel, 1 % Et_2O in pentane) afforded starting material **32** (238 mg, 25 %, $R_f=0.95$), and products **31** (471 mg, 47 %, $R_f=0.6$) and **33** (255 mg, 25 %, $R_f=0.4$). **33**: M.p. 182 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=4.13$ (t, $J=6.7$ Hz, 2 H; OCH_2), 1.63 (tt, $J=7.8$ Hz, 2 H; CH_2), 1.37 (tt, $J=7.5$ Hz, 2 H; CH_2), 0.93 (t, $J=8.5$ Hz, 3 H; CH_2CH_3), 0.11 (s, 9 H; $SiCH_3$), 0.08 (s, 15 H; BCH_3), 0.05 (s, 15 H; BCH_3), 0.02 (s, 15 H; BCH_3), 0.01 ppm (s, 15 H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=153.2$ (s; COO), 96.4 (s; ≡CSi), 94.9 (s; *C*≡CSi), 79.7 (s; *C*≡CCOO), 78.1 (s; ≡*C*COO), 76.4 (br s; carboranyl C), 76.0 (br s; carboranyl C), 74.2 (br s; carboranyl C), 73.1 (s; CC), 72.9 (br s; carboranyl C), 72.3 (s; CC), 71.8 (s; CC), 71.2 (s; CC), 66.3 (s; OCH_2), 30.5 (s; CH_2CH_2), 19.2 (s; CH_2CH_2), 13.9 (s; CH_2CH_3), 0.2 (s; $SiCH_3$), −4.6 ppm (br; BCH_3); ^{29}Si NMR (99.4 MHz, $CDCl_3$): $\delta=-16.9$ ppm (s); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, Et_2O): $\delta=-6.6$ ppm (br s, 20 B); HRMS (EI): *m*/*z*: calcd: 835.7774; found: 835.7766 [M^{+}]. **31**: M.p. 170 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=4.12$ (t, $J=6.8$ Hz, 4 H; OCH_2), 1.62 (tt, $J=7.8$ Hz, 4 H; CH_2), 1.36 (tt, $J=7.5$ Hz, 4 H; CH_2), 0.92 (t, $J=8.5$ Hz, 6 H; CH_2CH_3), 0.08 (s, 15 H; BCH_3), 0.04 ppm (s, 15 H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=153.1$ (s; COO), 79.8 (s; *C*≡CCOO), 78.1 (s; ≡*C*COO), 75.8 (br s; carboranyl C), 73.0 (br s; carboranyl C), 72.4 (s; CC), 72.0 (s; CC), 66.3 (s; OCH_2), 30.5 (s; CH_2CH_2), 19.2 (s; CH_2CH_2), 13.9 (s; CH_2CH_3), −4.5 ppm (br; BCH_3); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, pentane): $\delta=-6.6$ ppm (br s, 20 B); HRMS (EI): *m*/*z*: calcd: 863.7903; found: 863.7911 [M^{+}].

1-[12-Ethynyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1′-[12′-(*n*-butyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne (34): Compound **33** (440 mg, 0.500 mmol) was added to a slurry of $KF{\cdot}2H_2O$ (60.0 mg, 6.40 mmol) in DMF (20 mL) at 25 °C. The mixture was stirred for 8 h, and then quenched with water. The milky suspension was extracted with pentane (3×50 mL). The combined organic extracts were dried ($MgSO_4$) and purified by using flash chromatography on a bed of silica gel. Removal of the solvent provided **34** as a colorless solid (396 mg, 98 %). M.p. 138 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=4.13$ (t, $J=6.7$ Hz, 2 H; OCH_2), 2.47 (s, 1 H; CCH), 1.63 (tt, $J=7.8$ Hz, 2 H; CH_2), 1.36 (tt, $J=7.5$ Hz, 2 H; CH_2), 0.93 (t, $J=7.5$ Hz, 3 H; CH_2CH_3), 0.08 (s, 15 H; BCH_3), 0.05 (s, 30 H; BCH_3), 0.03 ppm (s, 15 H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=153.2$ (s; COO), 79.7 (s; *C*≡CCOO), 78.1 (s; ≡*C*COO), 77.04 (s; *C*≡CH), 76.0 (br s; carboranyl C), 75.3 (s; ≡CH), 74.8 (br s; carboranyl C), 74.6 (br s; carboranyl C), 72.9 (br s; carboranyl C), 72.8 (s; CC), 72.4 (s; CC), 72.2 (s; CC), 72.0 (s; CC), 71.4 (s; CC), 66.3 (s; OCH_2), 30.5 (s; CH_2CH_2), 19.2 (s; CH_2CH_2), 13.9 (s; CH_2CH_3), −4.6 ppm (br; BCH_3); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, pentane): $\delta=-6.7$ ppm (br s, 20 B); HRMS (EI): *m*/*z*: calcd: 763.7346; found: 763.7404 [M^{+}].

12,12′-{Bis[12-(*n*-butyl propiolyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)-1-(1,4-butadiynediyl)]}-1,1′-{bis[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne} (35): Compound **34** (350 mg, 0.460 mmol) was coupled by reacting CuCl (2.30 mg, 20.0 mmol), DBU (3.50 mL, 20.0 mmol), pyridine (20 mL), and oxygen over the course of 8 h at 25 °C. The solvent was removed in vacuo, dilute aqueous NH_4Cl was added, and the product was extracted with $CHCl_3$ (3×30 mL). The solution was passed through a bed of silica gel. The dried filtrate was recrystallized from hexane/benzene to afford **35** (312 mg, 89 %). M.p. 305 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=4.12$ (t, $J=6.8$ Hz, 4 H; OCH_2), 1.62 (tt, $J=7.8$ Hz, 4 H; CH_2), 1.35 (tt, $J=7.5$ Hz, 4 H; CH_2), 0.92 (t, $J=8.5$ Hz, 6 H; CH_2CH_3), 0.08 (s, 30 H; BCH_3), 0.04 (s, 30 H; BCH_3), 0.01 ppm (s, 60 H; BCH_3); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=153.2$ (s; COO), 79.7 (s; *C*≡CCOO), 78.1 (s; ≡*C*COO), 75.9 (br s; carboranyl C), 75.0 (br s; 2× carboranyl C), 72.9 (br s; carboranyl C), 72.7 (s; CC), 72.5 (s; CC), 72.2 (s; CC), 72.1 (s; CC), 71.8 (s; CC), 71.6 (s; CC), 66.3 (s; OCH_2), 30.5 (s; CH_2CH_2), 19.2 (s; CH_2CH_2), 13.9 (s; CH_2CH_3), −4.2 ppm (br; BCH_3); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, CH_2Cl_2): $\delta=-7.3$ ppm (br s, 40 B); MS data were unobtainable.

12,12′-{Bis[12-ethynyl-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)-1-(1,4-butadiynediyl)]}-1,1′-{bis[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne} (36): Compound **35** (250 mg, 0.160 mmol) and LiI (110 mg, 0.800 mmol) were heated under reflux in 2,6-lutidine (15 mL) for 8 h. Lutidine was distilled off and dilute aqueous HCl (10 mL) was added to the remaining residue. Extraction with benzene, subsequent filtration through a short bed of silica gel using benzene, and removal of the solvent afforded **36** as a colorless solid (208 mg, 98 %). M.p. >325 °C; ^{1}H NMR (400.13 MHz, 340 K, C_6D_6): $\delta=1.93$ (s, 2 H; CCH), 0.14 and 0.13 (2s, 90 H; BCH_3), −0.09, −0.08 ppm (2s, 90 H; BCH_3); ^{13}C NMR (100.62 MHz, 340 K, C_6D_6): $\delta=77.4$ (s, *C*≡CH) (br s; carboranyl C), 75.5 (br s; all carboranyl C), 75.2 (s; ≡CH), 73.9, 73.6, 73.4, 72.4, 72.2, 71.9 (s; CC), −4.2 ppm (br; BCH_3); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, benzene): $\delta=-7.3$ ppm (br s, 40 B); MS (FAB, negative mode): *m*/*z*: calcd: 1324.1; found: 1323.0 [M^{+}]; elemental analysis calcd for $C_{64}H_{122}B_{40}$: C 58.05, H 9.28; found: C 58.22, H 9.67.

1,12-Bis(2-formyl)-*closo*-1,12-dicarbadodecaborane(12) (38): To a solution of diol **37** (1.50 g, 7.30 mmol) in CH_2Cl_2 (10 mL), DMSO (5 mL), and Et_3N (12.3 mL, 88.0 mmol), a solution of sulfur trioxide–pyridine complex (7.00 g, 44.0 mmol) in DMSO (20 mL) was added. The reaction mixture was stirred at ambient temperature for 3 h and then partitioned between 5 % aqueous $NaHCO_3$ solution (30 mL) and Et_2O (30 mL). The aqueous phase was extracted with Et_2O (3×20 mL) and the combined ethereal extracts were washed with water and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the remaining residue was purified by using flash chromatography on a short bed of silica gel with Et_2O/petroleum ether (1:1). The dried eluant consisted of pure colorless **38** (0.99 g, 68 %). M.p. 288 °C (ref. [50]: 286–288 °C); ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta=8.79$ (s, 2 H; CHO), 3.10–1.70 ppm (m, 10 H; BH); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta=185.3$ (s; CHO), 84.6 ppm (s; carboranyl C); $^{11}B\{^{1}H\}$ NMR (160.46 MHz, Et_2O): $\delta=-14.2$ ppm (d, $J=150$ Hz, 10 B; BH).

1,12-Bis(2-chlorovinyl)-*closo*-1,12-dicarbadodecaborane(12) (39): At 0 °C, potassium *tert*-butoxide (1.14 g, 10.2 mmol) was added to a suspension of chloromethyl triphenylphosphonium chloride (3.75 g, 10.8 mmol) in THF (40 mL). The reaction mixture was stirred for 3 h at ambient temperature and then transferred into a solution of **38** (0.95 g, 4.70 mmol) in THF (10 mL) at 0 °C with a cannula. The reaction mixture was stirred for 5 h at ambient temperature. Water (30 mL) was added to the reaction mixture and the water phase was extracted with Et_2O (3×30 mL). The combined ethereal extracts were washed with water and dried over $MgSO_4$. After filtration, the solvent was removed from the filtrate under reduced pressure and the obtained residue was purified by using flash chromatography on a short bed of silica gel with pentane. Removal of the solvent in vacuo afforded **39** as a mixture of isomers (1.22 g, 98 %). ^{1}H NMR (400.13 MHz, CDCl$_3$): $\delta = 6.05$ (2d, $J = 13.3$ Hz, 1.1 H; CHCl), 5.91 (d, $J = 8.4$ Hz, 0.9 H; CHCl), 5.70 (2d, $J = 13.3$ Hz, 1.1 H; CH=), 5.37 (pseudo-t, $J = 8.5$ Hz, 0.9 H; CH=), 3.40–1.55 ppm (m, 10 H; BH); ^{13}C NMR (100.62 MHz, CDCl$_3$): $\delta = 130.6$, 130.4, 126.5, 126.3 (4s; CHCl), 123.6, 123.4, 120.7, 120.5 (4s; CH=), 78.4, 77.4, 76.4, 75.3 ppm (br, 4s; carboranyl C); ^{11}B{^{1}H} NMR (160.46 MHz, Et$_2$O): $\delta = -12.5$ ppm (d, $J = 158$ Hz; BH). Chromatography of **39** on silica gel using pentane afforded the majority of (*E*,*E*)-**39** (0.44 g, 35 %) as the first fraction ($R_f = 0.65$). M.p. 187 °C; ^{1}H NMR (500.13 MHz, CDCl$_3$): $\delta = 6.05$ (d, $J = 13.3$ Hz, 2 H; CHCl), 5.70 (d, $J = 13.3$ Hz, 2 H; CH=), 3.00–1.70 ppm (m, 10 H; BH); ^{13}C NMR (100.62 MHz, CDCl$_3$): $\delta = 130.4$ (s; CHCl), 123.6 (s; CH=), 76.4 ppm (br s; carboranyl C); ^{11}B{^{1}H} NMR (160.46 MHz, Et$_2$O): $\delta = -12.6$ ppm (d, $J = 158$ Hz; BH); IR (KBr) $\tilde{\nu} = 3082$, 2610, 1623, 1237, 1208, 1030, 923, 740, 650 cm^{-1}; HRMS (EI): *m*/*z*: calcd: 265.1458; found: 265.1471 [M^+].

1,12-Bis(ethynyl)-1,12-dicarbadodecaborane(12) (4): To a solution of **39** (1.06 g, 4.00 mmol) in THF (30 mL), a solution of *n*-butyllithium in hexanes (7.60 mL, 17.8 mmol, 2.35 M) was added dropwise at −18 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for an additional 2 h. The solvents were removed under reduced pressure and aqueous NaHCO$_3$ (30 mL) and petroleum ether were added to the residue. The water phase was extracted with petroleum ether (6 × 20 mL) and the combined organic extracts were dried over MgSO$_4$. After filtration through a short bed of silica gel the eluant was dried under reduced pressure and the obtained solid was sublimed at 50 °C/0.01 mm Hg (dry-ice cooled coldfinger) to yield pure **4** as a colorless solid (754 mg, 98 %). The melting point and the spectroscopic data for **4** were consistent with those published in the literature.[13] The UV spectrum of **4** in *n*-hexane does not exhibit any absorption maxima above 200 nm.

1,12-Bis(trimethylsilylethynyl)-*closo*-1,12-dicarbadodecaborane(12) (40): To a solution of **4** (0.120 g, 0.620 mmol) in THF (20 mL), a solution of methyllithium (1.00 mL, 1.40 mmol, 1.4 M in Et$_2$O) was added at 0 °C. The reaction mixture was stirred for 0.5 h at ambient temperature, cooled to −18 °C, and then chlorotrimethylsilane (0.190 mL, 1.50 mmol) was added. After the reaction mixture had been stirred for 1 h at ambient temperature, all volatiles were removed in vacuo and the residue was quenched with a dilute aqueous solution of NaHCO$_3$ (30 mL). The water phase was extracted with petroleum ether (3 × 20 mL), the combined organic extracts were dried over MgSO$_4$ and filtered through a short bed of silica gel. The dried eluant yielded **40** as a colorless solid (207 mg, 99 %). The melting point and the spectroscopic data for **40** were consistent with those published in the literature.[13] UV/Vis (*n*-hexane): $\lambda_{\max}$ ($\log\varepsilon$) = 198 nm (4.96).

1,12-Bis(trimethylsilylethynyl)-*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (41): To a solution of **11** (0.120 g, 0.360 mmol) in THF (20 mL), a solution of methyllithium (0.650 mL, 0.900 mmol, 1.4 M in Et$_2$O) was added at 0 °C. The reaction mixture was stirred for 0.5 h at ambient temperature, cooled to −18 °C, and chlorotrimethylsilane (0.150 mL, 1.20 mmol) was then added. After the reaction mixture had been stirred for 1 h at ambient temperature, all volatiles were removed in vacuo and the residue was quenched with a 5 % aqueous solution of NaHCO$_3$ (20 mL) and the water phase was extracted with hexanes (3 × 20 mL). The combined organic extracts were dried over MgSO$_4$, filtered through a short bed of silica gel, and dried under reduced pressure to yield **41** as a colorless solid (0.17 g, 99 %). M.p. 208 °C; ^{1}H NMR (400.13 MHz, CDCl$_3$): $\delta = 0.11$ (s, 9 H; SiCH$_3$), 0.01 ppm (s, 30 H; BCH$_3$); ^{13}C NMR (100.62 MHz, CDCl$_3$): $\delta = 96.7$ (s; ≡CSi), 94.3 (s; *C*≡CSi), 75.6 (br s; carboranyl C), −4.2 ppm (br; BCH$_3$); ^{11}B{^{1}H} NMR (160.46 MHz, Et$_2$O): $\delta = -9.1$ ppm (s); UV data contained no absorption maxima above 200 nm; HRMS (EI): *m*/*z*: calcd: 476.4311; found: 476.4292 [M^+].

Oligomerization of 29: Oxygen was bubbled through a mixture of **29** (1.00 g, 1.50 mmol), CuCl (7.40 mg, 70.0 mmol), and DBU (8.00 mL, 60.0 mmol) in pyridine (35 mL) for 5 h at 60 °C. After removal of all volatiles in vacuo, concentrated aqueous HCl was added and the mixture was extracted with hot toluene. The extracts were purified by using flash chromatography on a short bed of silica gel with toluene and the solvent was removed at 0.01 mm Hg at 180 °C. The residue was washed with pentane and dried to yield mixture **42[*n*]**. M.p. >350 °C; ^{1}H NMR (400.13 MHz, 66 °C, [D$_8$]toluene): $\delta = 1.96$ (s, 2 H; CCH), 0.09 (s, 120 H; BCH$_3$), 0.04 (s, 330 H; BCH$_3$), −0.00 ppm (s, 30 H; BCH$_3$); ^{13}C NMR (100.62 MHz, 66 °C, C$_6$D$_6$): $\delta = 77.4$ (s; C*C*H), 75.9–75.6 (br m; carboranyl C and CC), 74.2 (s; CC), 74.0 (m; CC), 72.6 (m; CC), −3.0 to −5.0 ppm (BCH$_3$); ^{11}B{^{1}H} NMR (160.46 MHz, benzene): $\delta = -7.2$ ppm (br s, 40 B); IR (KBr): $\tilde{\nu} = 3316$, 2951, 2909, 2835, 1728 (w), 1433 (w), 1322, 1162, 929 cm^{-1}; MS (EI) data was unobtainable.

***Trans*-bis[tri(*n*-butylphosphino)]-bis[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)-1-ethynyl]platinum(II) (46)**: To a solution of **17** (750 mg, 2.40 mmol), *cis*-dichloro-bis[tri(*n*-butylphosphino)]-platinum(II) (815 mg, 1.20 mmol), and Et$_2$NH (0.50 mL, 4.80 mmol) in CH$_2$Cl$_2$, CuI (10 mg, 0.050 mmol) was added and the mixture was stirred for 15 h at ambient temperature and finally gently heated at reflux for 0.5 h. All volatiles were removed in vacuo, water was added to the residue, and the crude product was extracted with hexanes. Chromatography on neutral Al$_2$O$_3$ using hexanes gave **46** as a colorless solid (1.00 g, 69 %, $R_f = 0.9$). M.p. 255 °C; ^{1}H NMR (400.13 MHz, CDCl$_3$): $\delta = 1.95$ (m, 12 H; PCH$_2$), 1.89 (s, 1 H; carboranyl CH), 1.40 (m, 24 H; PCH$_2$(C*H*$_2$)$_2$), 0.90 (t, $J = 7$ Hz, 18 H; CH$_2$C*H*$_3$), 0.03 (s, 15 H; BCH$_3$), 0.00 ppm (s, 15 H; BCH$_3$); ^{13}C NMR (100.62 MHz, CDCl$_3$): $\delta = 104.6$ (t, $J = 12.5$ Hz; PtC), 97.5 (s; PtC*C*), 80.7 (s; carboranyl C), 73.5 (br s; carboranyl C), 26.7 (s; CH$_2$), 24.3 (t, $J = 6$ Hz; CH$_2$), 23.1 (t, $J = 11$ Hz; CH$_2$), 14.4 (s; CH$_2$CH$_3$), −3.2 ppm (br; BCH$_3$); ^{31}P NMR (161.96 MHz, CDCl$_3$): $\delta = 2.9$ ppm (s); ^{11}B{^{1}H} NMR (160.46 MHz, Et$_2$O): $\delta = -5.9$ (s, 10 B), −9.3 ppm (s, 10 B); UV/Vis (*n*-hexane): $\lambda_{\max}$ ($\log\varepsilon$) = 208 (4.75), 255 (4.00), 269 (4.14), 304 nm (4.20); LRMS (EI): *m*/*z*: calcd: 1214.75; found: 1216.00 [M^+].

***Trans*-bis[tri(*n*-butylphosphino)]-bis{{1′-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranyl(12)]-1-[*closo*-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaboranylene(12)]-1,4-butadiyne}-12-ethynyl}-platinum(II) (47)**: The platinum complex **47** was synthesized in a manner analogous to the preparation of **46** but using **24** (198 mg, 0.300 mmol), *trans*-dichloro-bis[tri(*n*-butylphosphino)]platinum(II) (107 mg, 0.160 mmol), Et$_2$NH (66.0 mL, 0.640 mmol), and CuI (3.00 mg, 1.60 mmol) instead. Benzene was used for the product extraction and a mixture of benzene and CHCl$_3$ (2:1) was employed for chromatography on neutral Al$_2$O$_3$ to give **47** as a colorless solid (258 mg, 86 %). M.p. 330 °C (decomp); ^{1}H NMR (500.13 MHz, CDCl$_3$): $\delta = 2.05$ (s, 2 H; carboranyl CH), 1.93 (m, 12 H; PCH$_2$), 1.38 (m, 24 H; PCH$_2$(C*H*$_2$)$_2$), 0.89 (t, $J = 7$ Hz, 18 H; CH$_2$C*H*$_3$), 0.06 (s, 15 H; BCH$_3$), 0.01 (s, 15 H; BCH$_3$), −0.01 (s, 15 H; BCH$_3$), −0.03 ppm (s, 15 H; BCH$_3$); ^{13}C NMR (125.77 MHz, CDCl$_3$): $\delta = 106.2$ (t, $J = 12.5$ Hz; PtC), 98.2 (s; PtC*C*), 82.5 (s; carboranyl C), 76.4 (br s; carboranyl C), 73.6 (br s; carboranyl C), 73.1 (s; CC), 71.6 (br s; carboranyl C), 71.5 (s; CC), 71.3 (s; CC), 70.6 (s; CC), 26.7 (s; CH$_2$), 24.3 (t, $J = 6$ Hz; CH$_2$), 23.1 (t, $J = 11$ Hz; CH$_2$), 14.4 (s; CH$_2$CH$_3$), −3.2 (br; BCH$_3$), 4.3 ppm (br; BCH$_3$); ^{31}P NMR (202.45 MHz, CDCl$_3$): $\delta = 2.5$ ppm (s); ^{11}B{^{1}H} NMR (160.46 MHz, benzene): $\delta = -6.6$ (br s, 30 B), −9.4 ppm (s, 10 B); UV/Vis (*n*-hexane): $\lambda_{\max}$ ($\log\varepsilon$) = 208 (5.07), 243 (4.58), 271 (4.11), 306 nm (4.11); elemental analysis calcd for C$_{84}$H$_{176}$B$_{40}$P$_2$Pt: C 53.78, H 9.45; found: C 53.59, H 9.88.

1-Hydroxymethyl-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaborane(12) (50): To a solution of **48** (5.00 g, 19.5 mmol) in Et$_2$O (180 mL) at 0 °C, *n*BuLi (14.00 mL, 22.4 mmol, 1.6 M in pentane) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h. At −18 °C, solid paraformaldehyde (484 mg, 16.0 mmol) was added and the mixture was stirred for an hour while warming to room temperature. Saturated aqueous NaHCO$_3$ (50 mL) was added to the mixture. The aqueous phase was extracted with Et$_2$O (3 × 30 mL). The extracts were dried over MgSO$_4$, filtered, and the filtrate was dried under reduced pressure. Recrystallization of the residue from hexanes yielded **50** as a colorless solid (5.30 g, 95 %). M.p. 184 °C (decomp); ^{1}H NMR (400.13 MHz, CDCl$_3$): $\delta = 3.64$ (s, 2 H; CH$_2$), 2.30 (q, $J = 175$ Hz, 2 H; BH), 2.26 (s, 1 H; carboranyl CH), 1.96 (br s, 1 H; OH), 0.23 (s, 6 H; BCH$_3$), 0.12 (s, 6 H; BCH$_3$), −0.04 (s, 3 H; BCH$_3$), −0.15 (s, 6 H; BCH$_3$), −0.19 ppm (s, 3 H; BCH$_3$); ^{13}C NMR (100.61 MHz, CDCl$_3$): $\delta = 67.6$ (br s; carboranyl C), 60.0 (s; CH$_2$OH), 55.2 (br s; carboranyl C), −3.5 ppm (br; BCH$_3$); ^{11}B{^{1}H} NMR (160.46 MHz, Et$_2$O): $\delta = 2.3$ (s, 1 B), 1.5 (s, 1 B),

−2.3 (s, 2B), −6.3 (s, 2B), −7.5 (s, 2B), −17.6 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 286.3300; found: 286.3303 $[M^+]$.

1-Formyl-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaborane(12) (51): The oxidation of **50** as well as the purification of **51** were conducted as described for the synthesis of **9** (Scheme 2), **15** (Scheme 3), and **22** (Scheme 4), by using DMSO (4.86 mL, 68.4 mmol) and oxalyl chloride (3.00 mL, 34.2 mmol) in $\mathrm{CH_2Cl_2}$ (200 mL) at −62 °C. After the gas evolution had ceased, solid, anhydrous **50** (4.90 g, 17.1 mmol) was added at once and the reaction mixture was allowed to warm to −30 °C (1 h). The suspension was stirred at this temperature for 3 h and thereafter $i\mathrm{Pr_2NEt}$ (13.4 mL, 77.0 mmol) was added at −78 °C. At room temperature, all volatile components were removed in vacuum and the remaining residue was quenched with water (100 mL). The water layer was extracted twice with pentane (3×50 mL). The pentane of the combined organic layers was distilled off under reduced pressure and the obtained solid was purified by using flash chromatography on silica gel with $\mathrm{Et_2O}$/pentane (1:9). Removal of the solvent in vacuum afforded **51** (4.70 g, 98 %). M.p. 245 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=9.15$ (s, 1H; CHO), 2.42 (q, $J=172$ Hz, 2H; BH), 2.36 (s, 1H; carboranyl CH), 0.19 (s, 6H; $\mathrm{BCH_3}$), 0.17 (s, 6H; $\mathrm{BCH_3}$), 0.05 (s, 3H; $\mathrm{BCH_3}$), −0.01 (s, 3H; $\mathrm{BCH_3}$), −0.10 ppm (s, 6H; $\mathrm{BCH_3}$); ^{13}C NMR (100.61 MHz, $\mathrm{CDCl_3}$): $\delta=189.0$ (s; CHO), 69.7 (brs; carboranyl C), 55.3 (brs; carboranyl C), −3.9 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=3.3$ (s, 1B), 2.45 (s, 1B), −1.7 (s, 2B), −6.1 (s, 2B), −7.0 (s, 2B), −18.1 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 284.3141; found: 284.3149 $[M^+]$.

1-(2,2-Dibromovinyl)-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaborane(12) (52): A solution of **51** (4.60 g, 16.2 mmol), $\mathrm{CBr_4}$ (6.20 g, 18.7 mmol), and $\mathrm{PPh_3}$ (9.35 g, 35.6 mmol) in $\mathrm{CH_2Cl_2}$ (200 mL) was heated under reflux for 36 h. The solvent was removed under reduced pressure and the solid residue was triturated five times with dry $\mathrm{Et_2O}$. The combined ether extracts were evaporated and the residue was purified by using flash chromatography on silica gel with pentane. Removal of the pentane extract provided **52** (6.20 g, 87 %). The starting material **51** (460 mg, 10 %) was eluted from the column afterwards by using $\mathrm{Et_2O}$/pentane (1:8). M.p. 131 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=6.06$ (s, 1H; CH=), 2.75 (q, $J=190$ Hz, 2H; BH), 2.35 (s, 1H; carboranyl CH), 0.19 (s, 6H; $\mathrm{BCH_3}$), 0.10 (s, 6H; $\mathrm{BCH_3}$), 0.00 (s, 3H; $\mathrm{BCH_3}$), −0.07 (s, 3H; $\mathrm{BCH_3}$), −0.11 ppm (s, 6H; $\mathrm{BCH_3}$); ^{13}C NMR (100.61 MHz, $\mathrm{CDCl_3}$): $\delta=129.2$ (s; $\mathrm{CBr_2}$), 91.9 (s; CH=), 65.9 (brs; carboranyl C), 55.2 (brs; carboranyl C), −3.8 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=3.6$ (brs, 2B), −2.6 (s, 2B), −5.5 (s, 2B), −7.4 (s, 2B), −17.8 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 440.1545; found: 440.1533 $[M^+]$.

1-Ethynyl-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaborane(12) (53): To a freshly prepared suspension of $\mathrm{NaNH_2}$ (2.70 g, 69.0 mmol) in liquid ammonia (200 mL), a solution of dibromide **52** (6.00 g, 13.6 mmol) dissolved in $\mathrm{Et_2O}$ (100 mL) was transferred by using a cannula. The ammonia was allowed to evaporate. Dilute aqueous HCl (70 mL) was added to the remaining mixture at 0 °C and the products were extracted with pentane (2×50 mL). All volatiles were removed under reduced pressure and the remaining red solid was purified by using flash chromatography on silica gel with pentane. Removal of the solvent in vacuum afforded colorless **53** (2.98 g, 78 %). M.p. 272 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=2.75$ (q, $J=175$ Hz, 2H; BH), 2.28 (s, 1H; carboranyl CH), 2.24 (s, 1H; CCH), 0.20 (s, 12H; $\mathrm{BCH_3}$), −0.02 (s, 3H; $\mathrm{BCH_3}$), −0.10 ppm (s, 9H; $\mathrm{BCH_3}$); ^{13}C NMR (100.61 MHz, $\mathrm{C_6D_6}$): $\delta=77.1$ (s; $C{\equiv}$CH), 71.6 (s; C$\equiv$$C$H), 57.8 (brs; carboranyl C), 55.4 (brs; carboranyl C), −3.8 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=4.6$ (s, 1B), 2.9 (s, 1B), −1.7 (s, 2B), −4.5 (s, 2B), −6.8 (s, 2B), −15.3 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 280.3200; found: 280.3192 $[M^+]$.

1,1′-{Bis[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]}-1,4-butadiyne (54): Oxygen was passed through a mixture of **53** (2.30 g, 8.2 mmol), CuCl (40 mg, 0.4 mmol), and DBU (60 mL, 0.4 mmol) in anhydrous pyridine (120 mL) for 3 h at 45 °C. After removal of all volatiles in vacuo, an aqueous solution of $\mathrm{NaHCO_3}$ was added and the products were extracted with benzene. The benzene was removed by distillation and the remaining residue was purified by using flash chromatography on silica gel with pentane. The dried filtrate consisted of **54** (2.10 g, 91 %). M.p. >325 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=1.7$–3.2 (q, $J=175$ Hz, 4H; BH), 2.29 (s, 2H; carboranyl CH), 0.19 (s, 24H; $\mathrm{BCH_3}$), −0.03 (s, 6H; $\mathrm{BCH_3}$), −0.10 (s, 6H; $\mathrm{BCH_3}$), −0.12 ppm (s, 12H; $\mathrm{BCH_3}$); ^{13}C NMR (100.62 MHz, $\mathrm{CDCl_3}$): $\delta=72.1$ (s; CC), 66.3 (s; CC), 57.4 (brs; carboranyl C), 55.2 (brs; carboranyl C), −1.9 (br; $\mathrm{BCH_3}$), −3.8 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=4.8$ (s, 1B), 3.5 (s, 1B), −1.5 (s, 2B), −4.2 (s, 2B), −6.7 (s, 2B), −15.5 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 559.6215; found: 559.6195 $[M^+]$.

1-(7-Hydroxymethyl)-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]-1′-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]-1,4-butadiyne (55) and 1,1′-{bis[7-hydroxymethyl-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]}-1,4-butadiyne (56): To a cooled solution (0 °C) of **54** (2.00 g, 3.6 mmol) in a mixture of $\mathrm{Et_2O}$ (35 mL) and benzene (35 mL), nBuLi (1.06 mL, 1.6 M in $\mathrm{Et_2O}$, 1.7 mmol) was added. The solution was allowed to warm to room temperature and was then stirred for an additional hour. At 0 °C, solid paraformaldehyde (61 mg, 2.0 mmol) was added and the mixture was stirred for 1 h while warming it to room temperature. Saturated aqueous $\mathrm{NaHCO_3}$ (50 mL) was added and the aqueous phase was extracted with $\mathrm{Et_2O}$ (3×30 mL). The solvent of the combined organic layers was removed under reduced pressure. The residual product mixture was separated by using column chromatography (silica gel) first using pentane to recover unreacted **54** (440 mg, 22 %) then $\mathrm{Et_2O}$/pentane (1:3) to yield **55** (1.18 g, 56 %, $R_f=0.65$) and **56** (486 mg, 22 %, $R_f=0.3$) as colorless solids. Data for **55**: M.p. 319–323 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=3.65$ (s, 2H; $\mathrm{CH_2}$), 1.7–3.3 (q, $J=175$ Hz, 4H; BH), 2.29 (s, 1H; carboranyl CH), 1.65 (brs, 1H; OH), 0.21 (s, 6H; $\mathrm{BCH_3}$), 0.18 (s, 12H; $\mathrm{BCH_3}$), 0.16 (s, 6H; $\mathrm{BCH_3}$), −0.03 (s, 3H; $\mathrm{BCH_3}$), −0.07 (s, 3H; $\mathrm{BCH_3}$), −0.10 (s, 3H; $\mathrm{BCH_3}$), −0.12 (s, 12H; $\mathrm{BCH_3}$), −0.16 ppm (s, 3H; $\mathrm{BCH_3}$); ^{13}C NMR (100.62 MHz, $\mathrm{CDCl_3}$): $\delta=72.2$ (s; CC), 72.0 (s; CC), 67.1 (brs; carboranyl C), 66.3 (s; CC), 66.2 (s; CC), 59.9 (s; $\mathrm{CH_2OH}$), 57.4 (brs; carboranyl C), 57.4 (brs; carboranyl C), 56.7 (brs; carboranyl C), 55.2 (brs; carboranyl C), −3.9 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=2.3$ (s, 1B), 1.5 (s, 1B), −2.3 (s, 2B), −6.3 (s, 2B), −7.5 (s, 2B), −17.6 ppm (d, $J=175$ Hz, 2B; BH); HRMS (EI): m/z: calcd: 589.6321; found: 589.6327 $[M^+]$. Data for **56**: M.p. 386–392 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=3.67$ (s, 4H; $C$$H_2$OH), 2.55 (q, $J=175$ Hz, 4H; BH), 1.52 (s, 4H; $\mathrm{CH_2}$), 0.21 (s, 12H; $\mathrm{BCH_3}$), 0.17 (s, 12H; $\mathrm{BCH_3}$), −0.07 (s, 6H; $\mathrm{BCH_3}$), −0.1 (s, 12H; $\mathrm{BCH_3}$), −0.15 ppm (s, 12H; $\mathrm{BCH_3}$); ^{13}C NMR (100.62 MHz, $\mathrm{CDCl_3}$): $\delta=72.4$ (s; CC), 67.3 (brs; carboranyl C), 66.5 (s; CC), 66.0 (brs; carboranyl C), 60.1 (s; $\mathrm{CH_2OH}$), −3.9 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=2.3$ (s, 1B), 1.5 (s, 1B), −2.3 (s, 2B), −6.3 (s, 2B), −7.5 (s, 2B), −17.6 ppm (d, $J=175$ Hz, 2B; BH); IR (KBr): $\tilde{\nu}=3550$–3450 (OH), 2947, 2907, 2834, 2630, 1430, 1320, 1195, 1149, 1048, 933 cm^{-1}; HRMS (EI): m/z: calcd: 589.6321; found: 589.6327 $[M^+]$.

1,1′-{Bis[7-hydroxymethyl-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]}-1,4-butadiyne (56): Compound **56** was obtained quantitatively by reacting **54** with 2.2 equivalents of nBuLi in $\mathrm{Et_2O}$ and subsequently with paraformaldehyde (2.4 equiv). After the standard work up procedure the crude product was recrystallized from ethyl acetate.

1-(7-Formyl)-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]-1′-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]-1,4-butadiyne (57): The oxidation of **55** as well as the purification of **57** were conducted as described for the synthesis of **27**. Thus, reaction of DMSO (0.52 mL, 7.3 mmol), oxalyl chloride (0.32 mL, 3.7 mmol), **37** (1.08 g, 1.8 mmol), $i\mathrm{Pr_2NEt}$ (1.50 mL, 8.6 mmol), and $\mathrm{CH_2Cl_2}$ (150 mL) afforded **57** (1.04 g, 95 %). M.p. 239 °C; ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): $\delta=9.14$ (s, 1H; CHO), 3.4–1.6 (br, 4H; BH), 2.31 (s, 1H; carboranyl CH), 0.23 (s, 6H; $\mathrm{BCH_3}$), 0.19 (brs, 15H; $\mathrm{BCH_3}$), 0.08 (s, 3H; $\mathrm{BCH_3}$), −0.03 (brs, 6H; $\mathrm{BCH_3}$), −0.06 (s, 6H; $\mathrm{BCH_3}$), −0.09 (s, 6H; $\mathrm{BCH_3}$), −0.10 ppm (s, 6H; $\mathrm{BCH_3}$); ^{13}C NMR (100.62 MHz, $\mathrm{CDCl_3}$): $\delta=187.8$ (s; CHO), 72.8 (s; CC), 71.0 (s; CC), 69.0 (brs; carboranyl C), 67.2 (s; CC), 65.9 (s; CC), 57.2 (brs; 2× carboranyl C), 55.2 (brs; carboranyl C), −4.0 ppm (br; $\mathrm{BCH_3}$); ^{11}B{^{1}H-decoupled} NMR (160.46 MHz, $\mathrm{Et_2O}$): $\delta=6.5$ (s, 1B), 4.8 (brs, 3B), −1.2 (s, 4B), −3.6, −4.1, −4.9 (3s, 6B), −6.6 (s, 2B), −14.9 (s, 2B; BH), −15.3 ppm (s, 2B; BH); HRMS (EI): *m*/*z*: calcd: 587.6165; found: 587.6160 [M^++H].

1-[7-(2,2-Dibromovinyl)-*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]-1′-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]-1,4-butadiyne (58): Compound **58** was prepared and purified following the procedure described for the synthesis of **28**, by using **57** (900 mg, 1.5 mmol), CBr_4 (573 mg, 1.7 mmol), and PPh_3 (997 mg, 3.4 mmol) to yield the product (1.05 g, 94%). M.p. 103°C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 6.02$ (s, 1H; CH=), 3.75–1.75 (br, 4H; BH), 2.30 (s, 1H; carboranyl CH), 0.21 and 0.20 (2s, 18H; BCH_3), 0.12 (s, 6H; BCH_3), −0.02 (s, 3H; BCH_3), −0.04 (s, 3H; BCH_3), −0.06 (s, 3H; BCH_3), −0.06 ppm (brs, 15H; BCH_3); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 128.2$ (s; CBr_2), 92.9 (s; CH=), 72.3 (s; CC), 71.8 (s; CC), 66.6 (s; CC), 66.2 (s; CC), 65.3 (brs; carboranyl C), 57.3 (brs; carboranyl C), 57.0 (brs; carboranyl C), 55.2 (brs; carboranyl C), −1.9, −2.9, and −3.9 ppm (br; BCH_3); ^{11}B{^{1}H-decoupled} NMR (160.46 MHz, Et_2O): $\delta = 4.8$ (m, 4B), −1.7 (s, 4B), −4.3 (s, 5B), −6.7 (s, 3B), −14.5 (s, 1B; BH), −15.5 ppm (s, 3B; BH).

1-[7-Ethynyl-closo-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]-1′-[closo-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]-1,4-butadiyne (59): Compound **59** was prepared and purified following the procedure described for the synthesis of **29**, by using **58** (950 mg, 1.3 mmol) and a freshly prepared suspension of $NaNH_2$ (293 mg, 7.5 mmol) in ammonia (70 mL) to afford colorless **59** (647 mg, 85%). M.p. 294°C; ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 3.40$–1.50 (br, 4H; BH), 2.30 (s, 1H; carboranyl CH), 2.27 (s, 1H; CCH), 0.23 (s, 12H; BCH_3), 0.20 (s, 12H; BCH_3), 0.01 (s, 3H; BCH_3), 0.06 (s, 3H; BCH_3), 0.07 (brs, 15H; BCH_3), 0.09 ppm (s, 3H; BCH_3); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 76.1$ (s; CCH), 72.5 (s; CC), 71.7 (s; CC), 71.4 (s; CC), 66.7 (s; CC), 66.1 (s; CC), 57.3 (brs; carboranyl C), 56.9 (brs; carboranyl C), 56.7 (brs; carboranyl C), 55.3 (brs; carboranyl C), 1.9, 2.9, and 3.9 ppm (br; BCH_3); ^{11}B{^{1}H} NMR (160.46 MHz, Et_2O): $\delta = 5.1$ (s, 3B), 4.2 (s, 1B), −1.6 (s, 4B), −4.3 (s, 6B), −6.6 (s, 2B), −12.9 (d, $J = 175$ Hz, 2B; BH), −15.4 ppm (d, $J = 175$ Hz, 2B; BH); HRMS (EI): *m*/*z*: calcd: 583.6216; found: 583.6209 [M^+].

7,7′-{Bis{1-[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranyl(12)]-1,4-butadiynediyl}}-{1,1′-{bis[*closo*-4,5,6,8,9,10,11,12-octamethyl-1,7-dicarbadodecaboranylene(12)]}-1,4-butadiyne} (60): Compound **59** (500 mg, 0.84 mmol) was coupled in a manner analogous to the synthesis of **54** by using CuCl (4 mg, 42 mmol), DBU (0.2 mL, 1.3 mmol), pyridine (50 mL), and oxygen. The crude product was purified by using flash chromatography on a short bed of silica gel with benzene and the dried filtrate was recrystallized by using pentane to yield **60** as a colorless solid (449 mg, 90%). M.p. >325°C; ^{1}H NMR (500.13 MHz, 100°C, [D_8]toluene): $\delta = 2.33$ (q, $J = 175$ Hz, 4H; BH), 1.59 (s, 2H; carboranyl CH), 0.24 (s, 6H; BCH_3), 0.21 (s, 6H; BCH_3), 0.20 (s, 6H; BCH_3), 0.06 (s, 6H; BCH_3), −0.01 (s, 3H; BCH_3), −0.03, −0.04, −0.06, −0.03 (s, 18H; BCH_3), −0.11 ppm (s, 3H; BCH_3); ^{13}C NMR (125.77 MHz, 100°C, [D_8]toluene): $\delta = 74.2$ (s; CC), 73.1 (s; CC), 72.4 (s; CC), 67.8 (s; CC), 67.5 (s; CC), 66.8 (s; CC), 58.1 (brs; carboranyl C), 57.9 (brs; carboranyl C), 57.7 (brs; carboranyl C), 55.9 (brs; carboranyl C), −2.8 and −3.8 ppm (br, BCH_3); ^{11}B{^{1}H} NMR (160.46 MHz, benzene): $\delta = 4.8$ (brs, 4B), 3.6 (brs, 2B), −1.8 (s, 9B), −4.4 (s, 9B), −7.2 (s, 6B), −12.4 (brd, 2B; BH), −15.9 ppm (d, $J = 175$ Hz, 6B; BH); MS (EI): *m*/*z*: calcd: 1157.838; found: 1157.83 [M^+].

CCDC-262361 (**30**), CCDC-262362 (**40**), and CCDC-262363 (**41**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[37] X-ray data of **30**: $C_{40}H_{74}B_{20}O_6$; $M_r = 867.19$; monoclinic space group $P2_1/n$; $a = 11.628(3)$, $b = 13.285(4)$, $c = 18.028(6)$ Å; $\beta = 108.546(5)^\circ$; $V = 2640.2(14)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.091$ mg mm^{-3}; $\mu = 0.063$ mm^{-1}; $F(000) = 924$. A colorless crystal (parallelepiped, $0.2 \times 0.25 \times 0.5$ mm^3), obtained from a solution of the crystal in ethyl acetate, was used for data collection (Bruker SMART CCD-diffractometer, $Mo_{K\alpha}$ radiation) at $T = 100$ K ($2\theta_{max} = 56.56^\circ$) giving 5998 unique reflections. The structure was solved by direct methods. The final discrepancy indices were $R = 0.060$ and $R_w = 0.156$ for 2995 independent reflections with $I > 2\sigma(I)$ (goodness-of-fit on $F^2 = 0.915$). The maximum and minimum values on a final difference electron density map were 0.303 and -0.259 e Å^{-3}. The asymmetric unit contains one half molecule of **30** and one half molecule of ethyl acetate. The rod molecule is centrosymmetric and the ethyl acetate is disordered

about a center of symmetry. All non-hydrogen atoms were included with anisotropic displacement parameters. All hydrogen atoms were kept in calculated positions.

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[39] X-ray data of **41**: $C_{22}H_{48}B_{10}Si_2$; $M_r = 476.88$; triclinic space group $P\text{-}1$; $a = 9.342(2)$, $b = 9.456(2)$, $c = 9.996(2)$ Å; $\alpha = 93.795(4)$, $\beta = 99.424(4)$, $\gamma = 116.561(3)°$; $V = 769.4(3)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.029$ mg mm^{-3}; $\mu = 0.126$ mm^{-1}; $F(000) = 258$. A colorless crystal (parallelepiped, $0.4 \times 0.5 \times 0.5$ mm^3), obtained from a solution of the crystal in pentane, was used for data collection (Bruker SMART CCD-diffractometer, $Mo_{K\alpha}$ radiation) at $T = 100$ K ($2\theta_{max} = 56.6°$) giving 3599 unique reflections. The structure was solved by direct methods. The final discrepancy indices were $R = 0.041$ and $R_w = 0.119$ for 3074 independent reflections with $I > 2\sigma(I)$ (goodness-of-fit on $F^2 = 1.086$). The maximum and minimum values on a final difference electron density map were 0.435 and -0.303 e Å^{-3}. Atoms were located by use of statistical methods. The asymmetric unit contains one half molecule of **41** and the molecule is centrosymmetric. All non-hydrogen atoms were included with anisotropic displacement parameters. All hydrogen atoms were kept in calculated positions.

[40] X-ray data of **40**: $C_{12}H_{28}B_{10}Si_2$; $M_r = 336.62$; monoclinic space group $C2/m$; $a = 21.708(4)$, $b = 7.5271(15)$, $c = 6.9299(14)$ Å; $\beta = 107.750(4)°$; $V = 1078.4(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.037$ mg mm^{-3}; $\mu = 0.156$ mm^{-1}; $F(000) = 356$. A colorless crystal (plate, $0.03 \times 0.4 \times 0.5$ mm^3), obtained from a pentane solution, was used for data collection (Bruker SMART CCD-diffractometer, $Mo_{K\alpha}$ radiation) at $T = 100$ K ($2\theta_{max} = 56.58°$) giving 1409 unique reflections. The structure was solved by direct methods. The final discrepancy indices were $R = 0.034$ and $R_w = 0.092$ for 1124 independent reflections with $I > 2\sigma(I)$ (goodness-of-fit on $F^2 = 1.021$). The maximum and minimum values on a final difference electron density map were 0.338 and -0.332 e Å^{-3}. The asymmetric unit contains one quarter molecule **40** and the molecule has $2/m$ symmetry. All non-hydrogen atoms were included with anisotropic displacement parameters. All hydrogen atoms were kept in calculated positions.

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