The Synthesis of Carboracycles Derived from *B,B′*-Bis(aryl) Derivatives of Icosahedral *ortho*-Carborane

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Abstract: Reactions of both *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ and *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ with an excess of aryl magnesium bromide in the presence of $[PdCl_2(PPh_3)_2]$ afford the corresponding *closo*-9,12-(4-R-C_6H_4)$_2$-1,2-$C_2B_{10}H_{10}$ [R = H (**1**), Me (**2**), OMe (**3**), SMe (**4**), $N(CH_3)_2$ (**5**), Cl (**6**)] and *closo*-9,10-(4-R′-C_6H_4)$_2$-1,7-$C_2B_{10}H_{10}$ [R′ = Me (**7**), OMe (**8**), $N(CH_3)_2$ (**9**), Cl (**10**), and -C[$(OCH_2)_2$]CH_3 (**11**)] compounds in high yields. The anisole derivatives **3** and **8** were deprotected to yield the corresponding bis-phenols **12** and **13**, respectively. Structural analyses of compounds **1**, **3**, **6**, and **12** are reported. Reetherification of compound **12** by using γ-bromotriethyleneglycol methyl ether provided **14** (R = $(CH_2CH_2O)_3CH_3$). Oxidation of **4** with ceric(IV) ammonium nitrate (CAN) generated the bis-sulfoxide **15** (R = S(O)Me). Deprotection of compound **11** led to the corresponding acetyl derivative **18** (R′ = C(O)Me). Bisanisole **3** was tethered with 1,3-dibromopropane, 1,6-dibromohexane, 1,8-dibromooctane, 4,4′-bis(iodomethyl)-1,1′-biphenyl, and α,α'-dibromo-2,6-lutidine to afford the dimers **20b**, **21b**, **22b**, **23b**, and **24b**, respectively. The tetrameric carboracycles **27a** and **30a**, as well as the dimeric **29c** were obtained through repetitive coupling of the dimeric compounds **20b**, **24b**, and **22b** with 1,3-dibromopropane, α,α'-dibromo-2,6-lutidine, and 1,8-dibromooctane, respectively. The tetrameric carboracycle **28a** was obtained upon consecutive reactions of **1** with 1,4-dibromobutane. Hexameric carboracycle **28b** was identified as a byproduct. Exhaustive ether cleavage of **27a** generated octaphenol **31a**. Reetherification of **31a** with trimethylenesultone provided the octasulfonate **32a**, the first example of a water-soluble carboracycle. Linkage of dimer **23b** with α,α'-dibromolutidine yielded the cyclic tetrameric tetrapyridyl derivative **30a** in low yield. The structures of the carboracycles **27a**, **28a**, **28b**, and **30a** have been confirmed by X-ray crystallography. In addition, the compounds **28a**,**b** are the first reported carboracycles that interact with solvent molecules in a host–guest fashion.

Keywords: boron · carboracycles · carboranes · host–guest chemistry · macrocycles

Introduction

Due to their rigid near-spherical geometry and their chemical and thermal stabilities the icosahedral carboranes ($C_2B_{10}H_{12}$) can serve as chemical building blocks for several specialized applications in the field of biomedical and material sciences.[1–8] The design and synthesis of macromolecular architectures which employ icosahedral carborane cages as integral modules has only recently been explored.[8b, 9–16] Assemblies such as mercuracarborands,[12] carboracycles[13, 14] and carborarods[15] are tailored to exploit the versatile chemistry of the carborane C–H and B–H vertices along with the rigid three-dimensional nature of the three isomeric icosahedral *closo*-carborane cages (1,2-, 1,7- and 1,12-). However, frameworks composed of carboranes that bear substituents at both the C and B vertices are rare,[17] since these scaffolds are commonly constructed utilizing the carbon vertices of the parent carboranes. However, cage substituents such as alkyl are typically placed at the boron vertices to improve the solubility of the macromolecule in organic solvents. Seldom do they play a role in a multifunctional construct.[3a, 18]

To date, the reaction of B-iodinated polyhedral boranes with a Grignard reagent under Kumada coupling conditions[19] can be considered to be the most reliable route to B–C-substituted species[20] and a library of B-alkylated, -ethynylated, and -arylated carborane derivatives was obtained by this method. However, the vast majority of these coupling reactions afford carborane derivatives with B-hydrocarbon residues, and only in the case of B-arylation has the direct introduction of functionalized hydrocarbon residues been achieved.

Here we have extended the family of icosahedral *B,B′*-bis(diaryl) *closo*-1,2- and *closo*-1,7- icosahedral carboranes to those compounds bearing functional groups in the 4-position

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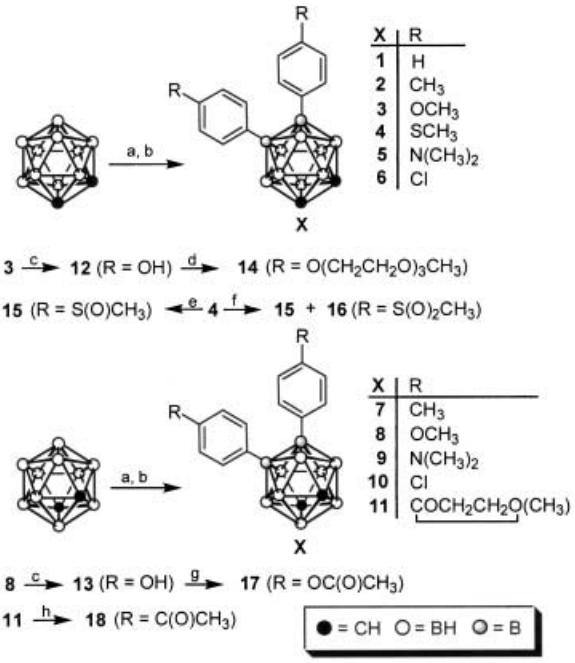
of their substituted phenyl groups. In addition, we describe their incorporation into cyclic macromolecular arrays; this in turn allows their derivatization, which results in such unusual properties such as water-solubility.[21] Related structure determinations, including that of the first hexameric carboracycle, are reported.

Results and Discussion

Synthesis and reactivity of icosahedral *closo*-*B*,*B*′-bis(aryl) carboranes: Following previously applied protocols, *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$[20a] and *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$[20a] were first deprotonated with one equivalent of methyl magnesium bromide (which was used to neutralize one of the two acidic carborane C–H vertex protons) and thereafter arylated using 3.5 equivalents of freshly prepared aryl magnesium bromide in the presence of $[PdCl_2(PPh_3)_2]$ (3 mol%) (Scheme 1). The yields of the coupled products were all good to excellent.



Scheme 1. B-Arylation of 1,2- and 1,7-carborane: a) ICl, $AlCl_3$, CH_2Cl_2; b) 1. MeMgBr 2. R′MgBr (R′ = 4-R-aryl), $PdCl_2(PPh_3)_2$; c) BBr_3; d) K_2CO_3, $Br(CH_2CH_2O)_3CH_3$; e) $(NH_4)_2Ce(NO_3)_6$, $(n\text{Bu})_4\text{NBr}$; f) *m*-chloroperbenzoic acid; g) $(Ac)_2O$; h) HCl (10%).

The bis-4-methoxyphenyl derivatives **3** and **8** were efficiently deprotected regiospecifically by using BBr_3 to furnish the phenol derivatives *closo*-9,12-(4-$C_6H_4OH)_2$-1,2-$C_2B_{10}H_{10}$ (**12**) and *closo*-9,10-(4-$C_6H_4OH)_2$-1,7-$C_2B_{10}H_{10}$ (**13**), respectively, in quantitative yields.[22] In the solid state, the diols contain one molecule of polar solvent such as diethyl ether (vide infra), acetone, or THF, even after drying at elevated temperatures in vacuo. Diol **12** was further reacted to give the bis-monomethyltriethylene glycolether derivative **14** (Scheme 1). The etherification was conducted under standard conditions[23] by using 2-bromoethylene di(ethyleneglycol) methyl ether[24] under mild basic conditions (K_2CO_3) (Scheme 1). The product formed in only 75% yield due to incomplete alkylation; degradation of the carborane cage was not observed. Compound **14** was insoluble in water.

The selective oxidation of **4** proved difficult. While the reaction of **4** with two equivalents of urea-hydrogen peroxide adduct in acetone did not occur at all, oxidation of **4** with *m*-CPBA[25] or MnO_2[25] resulted in the formation of the desired bis-sulfoxide **15** only in low yield accompanied by the generation of the bis-sulfone derivative **16**. Almost quantitative yield of **15** was obtained upon the reaction of **4** with four equivalents of CAN[26] under phase-transfer conditions (Scheme 1).

The quarternization and protonation of both **5** and **9** were attempted, but their reactions with methyl iodide and trifluoromethyl sulfonic acid, respectively, did not generate the corresponding ammonium species.

Both the reactions of bis-phenol **13** with β-1,2,3,4-tetraacetyl-6-tosyl-D-glucose[27] and β-1,2,3,4-tetraacetyl-6-iodo-D-glucose,[27] respectively, in the presence of K_2CO_3 (acetone) or *n*BuLi (THF) resulted in transesterification affording the diacetate **17** (74%). The same reactions carried out in CH_3CN (K_2CO_3) resulted in the degradation of **17**, based on ^{11}B NMR spectroscopy and FAB mass spectrometry data. However, isolation of this *nido*-species was not attempted. Compound **17** was obtained in quantitative yield by treating **13** with acetic anhydride in the presence of triethylamine.

The reaction of ketal **11** with 10% HCl resulted in the formation of **18** (Scheme 1).

Structural characterizations: Compounds **1**, **3**, **6**, and **12** were structurally characterized (Table 1). Their X-ray crystal structures (Figures 1–4) indicate that infinite polymeric chains are formed in the solid state; in all cases they are imposed by weak non-classical carborane C–H···π hydrogen bonding as observed previously.[20c, 28] Each polarized carborane C–H is directed towards the centroid of an aromatic ring of an adjoining molecule by interaction with the π-electrons of the aromatic ring.

In the structure of **1** (Figure 1) the C···π centroid separations are 3.35 and 3.74 Å and the C–H···π angles are 171 and 173°, respectively. The π···C1–C2···π dihedral angle for **1** measures 0°, suggesting that the molecule packs in the crystal lattice without any apparent distortions to the icosahedral carborane cage.

In the crystal structure of **3** (Figure 2) C···π centroid separations are 3.31 and 3.33 Å and C–H···π angles are 167.7 and 167.9°, respectively. The π···C1–C2···π dihedral angle of 2.5° indicates almost distortion-free crystal packing of compound **3**.

The crystal structure of compound **6** (Figure 3) reveals C···π centroid separations of 3.55 (C1A···π), 3.53 (C2A···π), 3.49 (C1B···π), and 3.52 Å (C2B···π) and C–H···π angles of 166.5, 174.3, 170.2, and 170.1°, respectively. The dihedral angles of 9.1 (π···C1A–C2A···π) and 10.7° (π···C1B–C2B ···π) indicate a significant distortion of the icosahedron.

In the crystal structure of **12** (Figure 4), which contains one molecule of diethyl ether per carborane unit, the C···π centroid separations are 3.40 and 3.49 Å and C–H···π angles

Table 1. Crystallographic data and details of the structure determinations of compounds **1**, **3**, **6**, and **12**.

	1	**3**	**6**	**12**
formula	$C_{14}H_{20}B_{10}$	$C_{32}H_{48}B_{20}O_4$	$C_{56}H_{72}B_{40}Cl_8$	$C_{36}H_{60}B_{20}O_6$
M_r	296.40	712.90	1461.14	805.04
T [K]	293(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$C2/c$	$P2_1/c$
a [Å]	18.096(16)	6.938(4)	27.402(8)	11.168(11)
b [Å]	7.711(6)	14.917(8)	16.451(5)	15.732(17)
c [Å]	14.229(12)	19.560(10)	21.671(7)	13.563(15)
α [°]	90	90	90	90
β [°]	122.68(2)	90.89(2)	128.190(7)	96.75(3)
γ [°]	90	90	90	90
V [Å^3]	1671(2)	2024.0(2)	7678(4)	2366(4)
Z	4	2	16	4
ρ_{calcd} [g cm^{-3}]	1.178	1.170	1.264	1.130
μ [mm^{-1}]	0.404	0.065	0.332	0.501
$F(000)$	616	744	2976	848
crystal size [mm]	$0.20 \times 0.22 \times 0.40$	$0.22 \times 0.28 \times 0.40$	$0.38 \times 0.20 \times 0.18$	$0.45 \times 0.15 \times 0.10$
θ_{max} [°]	57.50	30.00	27.50	57.47
index ranges	0/19, 0/8, −15/13	0/9, 0/19, −27/27	0/35, 0/19, −25/20	0/12, 0/17, −14/14
unique reflections	1141	4923	7138	3231
reflections observed [$I > 2\sigma(I)$]	966	1918	2952	1595
parameters	115	266	370	245
$R1$ [$I > 2\sigma(I)$]	0.0460	0.0628	0.0603	0.0780
$wR2$	0.1229	0.2010	0.1895	0.2477
largest diff. peak/hole [e Å^{-3}]	+0.198/−0.161	+0.274/−0.191	+0.304/−0.245	+0.235/−0.246

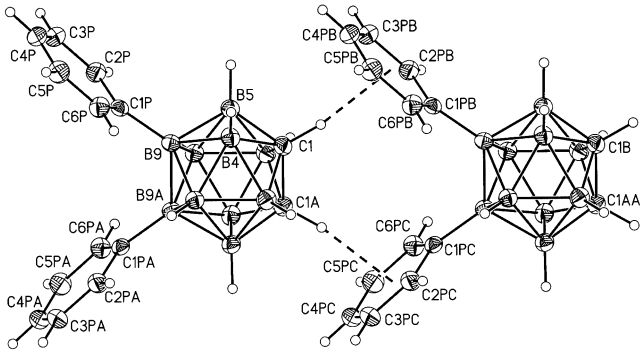


Figure 1. ORTEP representation showing the molecular structure of **1**.

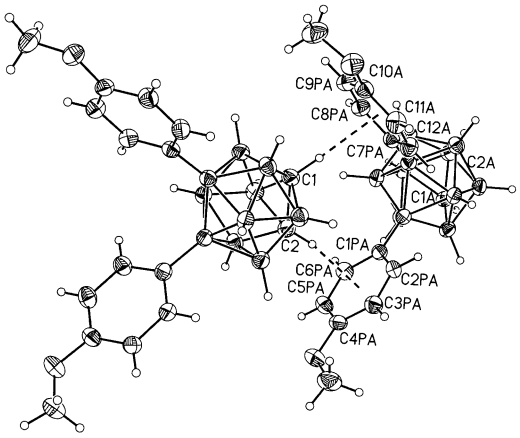


Figure 2. ORTEP representation showing the molecular structure of **3**.

are 172.9 and 167.9°, respectively. The π···C1−C2···π dihedral angle of 2.5° is identical to that of **3**, indicating only a slight dihedral angle distortion. The crystal packing of **12** is

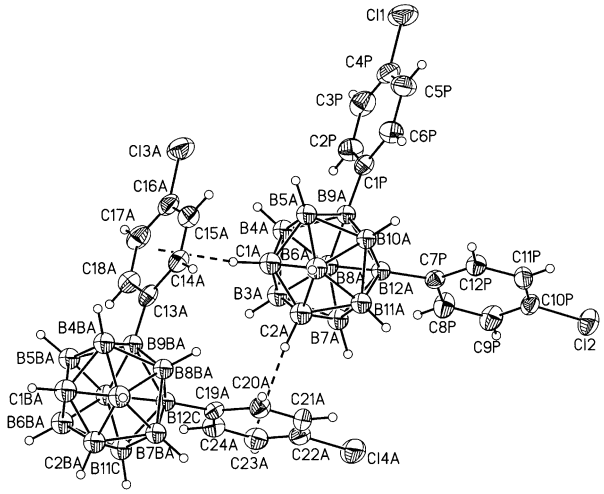


Figure 3. ORTEP representation showing the molecular structure of **6**.

also affected by classical intermolecular O−H···O hydrogen-bonding interactions between the phenyl hydroxyl groups. In addition, hydrogen bridges are formed between the solvent oxygen atoms and hydroxyl groups.

The carborane C−H···π interactions in the solid-state structures of **1**, **3**, **6**, and **12** are also reflected in their IR spectra. The stretching frequencies for the carboranyl C−H bonds of **1** (3069 cm^{-1}), **3** (3069 and 3065 cm^{-1}), **6** (3067 cm^{-1}), and **12** (3064 cm^{-1}) are shifted to lower wavenumbers relative to those of *ortho*-carborane (3071 cm^{-1}). This phenomenon is consistent with previous observations.[20c, 28a, 29] In addition, the infrared spectrum of **12** displays two distinct O−H stretching modes at 3497 and 3383 cm^{-1} in agreement with its two different types of bridging OH-substituents (vide supra).

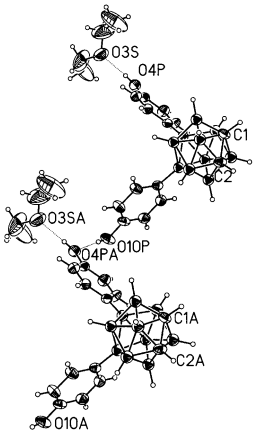
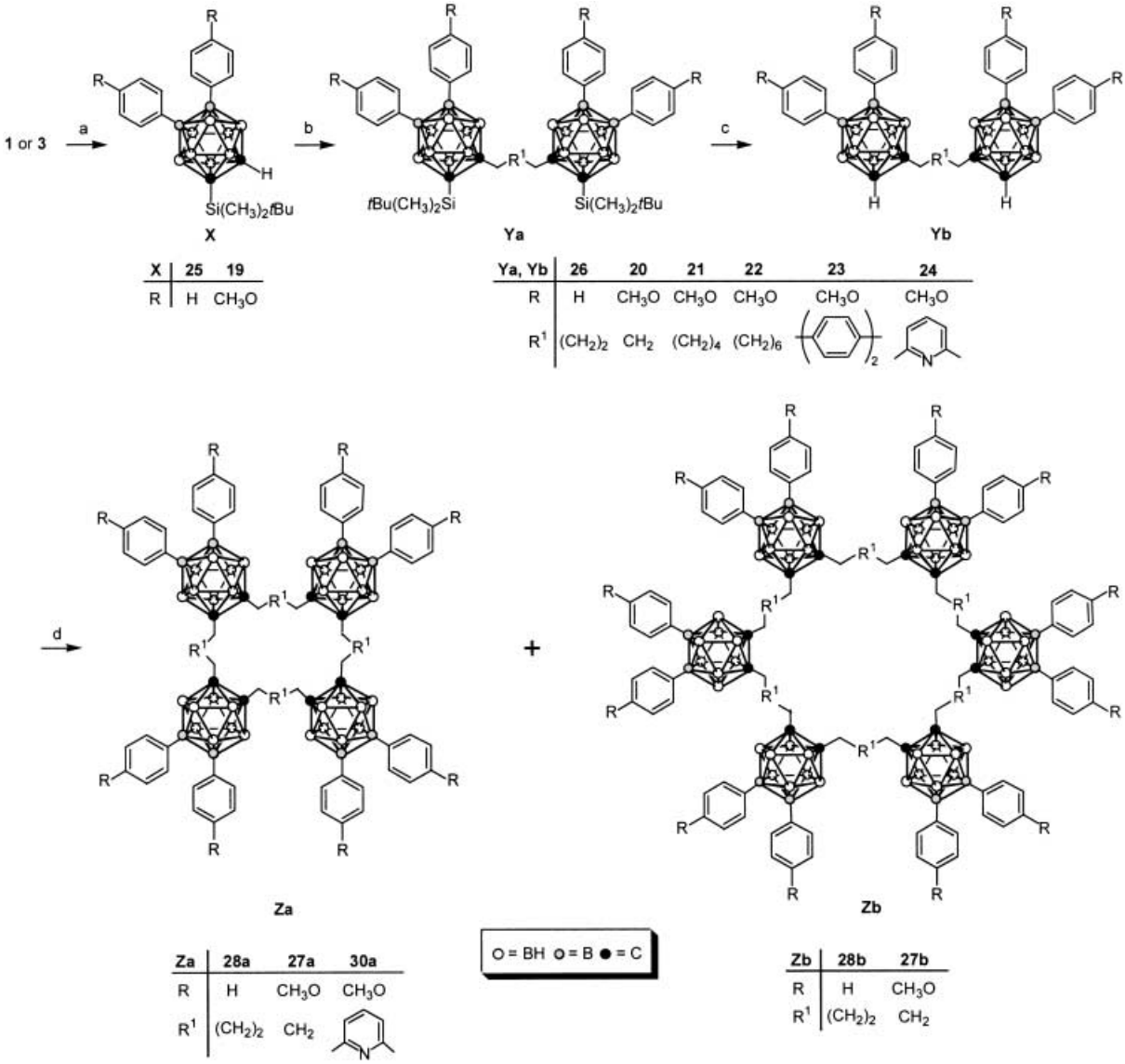


Figure 4. Crystal structure of **12** illustrating the carborane C–H···π interactions and the O4PA···O3SA separation of 2.66 Å, the O4PA···O10P separation of 2.78 Å; the O4PA–H···O3SA angle of 161.2°, and the O4PA···H–O10P angle of 177.0°.

Synthesis of multifunctional carboracycles: Bis-anisole **3** was chosen for the syntheses of the functionalized carboracycles. In the first step, a linkage between two substituted *closo*-1,2-carborane molecules was established by protecting regioselectively one of the two C–H vertices of the carborane with a *tert*-butyldimethylsilyl group,[30] followed by deprotonation of the second C–H vertex and subsequent reaction with an appropriate dihalide (Scheme 2).[13] The employment of 1,3-dibromopropane, 1,6-dibromohexane, 1,8-dibromooctane, 4,4′-bis(iodomethyl)-1,1′-biphenyl, and α,α'-dibromo-2,6-lutidine, respectively, afforded the bis-protected dimeric building blocks **20a**, **21a**, **22a**, **23a**, and **24a** in 80–90% yields. Desilylation of the dimers was achieved with tetrabutylammonium fluoride to provide the compounds **20b**–**24b** in quantitative yields (Scheme 2).

The tetrameric carboracycle **27a** was obtained upon bislithiation of **20b** with *n*-butyllithium and subsequent reaction with 1,3-dibromopropane (Scheme 2).[13] Due to the 4-methoxy phenyl substituents, compound **27a** exhibits enhanced



X	25	19
R	H	CH_3O

Ya, Yb	26	20	21	22	23	24
R	H	CH_3O	CH_3O	CH_3O	CH_3O	CH_3O
R^1	$(CH_2)_2$	CH_2	$(CH_2)_4$	$(CH_2)_6$		

Za	28a	27a	30a
R	H	CH_3O	CH_3O
R^1	$(CH_2)_2$	CH_2	

Zb	28b	27b
R	H	CH_3O
R^1	$(CH_2)_2$	CH_2

Scheme 2. Synthesis of various carboracycles: a) 1. *n*BuLi, 2. TBDMSCl; b) 1. *n*BuLi, 2. $HalCH_2R^1CH_2Hal$; c) $(nBu)_4NF$; d) 1. *n*BuLi, 2. $HalCH_2R^1CH_2Hal$.

solubility in common organic solvents compared to the corresponding unsubstituted species.[13] Thus **27a** could be characterized unambiguously by NMR mspectroscopy. Compared to the ^{11}B NMR spectrum of **20a**, in which four distinct peaks in the ratio of 1:1:2:6 were observed, the spectrum of **27a** exhibits two broad signals in the ratio of 1:4, a characteristic pattern found for a carboracycle containing 1,2-carborane.[13] Mass spectrometric analysis of **27a** displayed the parent peak ($m/z = 1586.4$) by applying FAB (positive mode). However, the mass spectra of samples of the crude reaction mixture, as well as the solid residues of impure **27a** retained from multiple recrystallizations, consistently exhibit a peak with an intensity of 30% at $m/z = 2379.8$. Both its mass range and isotope pattern were consistent with that expected for the hexameric carboracycle **27b**. Unfortunately, species **27b** could be isolated neither by recrystallization nor by column chromatography.

Crystals of compound **27a** suitable for X-ray structure analysis (Table 2) were grown from a solution in 1,3-dimethoxybenzene. The centrosymmetric structure of **27a** is depicted in Figure 5. The macrocycle possesses a chair conformation. Four carborane cages and two opposing trimethylene linkers describe a plane, while the remaining two linkers lie above and below the plane of the cyclic tetramer, respectively.

Comparable to the synthesis of **27a**, the analogous preparation of tetrameric carboracycle **28a** from **1** and 1,4-dibromobutane (Scheme 2) was also accompanied by the formation of the corresponding hexameric species **28b** (Scheme 2), based on ^{11}B NMR data. Separation of **28a** from **28b** was achieved by fractional crystallization from 1,3-dimethoxybenzene to give pure **28a** in 79% yield. The product was characterized by NMR spectroscopy, mass spectrometry, and X-ray analysis (Table 2). The hexameric

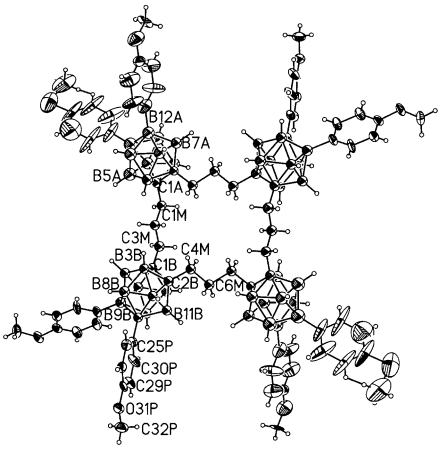


Figure 5. ORTEP representation showing the molecular structure of **27a**.

carboracycle **28b**, which, like **27b**, formed only in minor amounts, was identified by mass spectrometry. Additionally, the X-ray analysis of **28b** could be performed with single crystals obtained by multiple recrystallization of the mixture of **28a** and **28b** in 1,3-dimethoxybenzene and final manual separation based on morphological features.

Colorless crystals of **28a** suitable for an X-ray diffraction study were obtained from a solution of 1,4-dioxane. The structure is shown in Figure 6. The carborane cages of the macrocycle share a common plane, while the four tetramethylene linkers are alternately bent above and below the plane of the molecule; the macrocycle has S_4 symmetry. The crystal contains six molecules of 1,4-dioxane per cyclic tetramer; two of them are severely disordered while the remaining four are disordered at the oxygen atoms. Remark-

Table 2. Crystallographic data and details of the structure determinations of compounds **27a**, **28a**, **28b**, and **30a**.

	27a·2(CH$_3$O)$_2$C$_6$H$_4$	**28a**·6(C$_2$H$_4$O$_2$)$_2$	**28b**·8(CH$_3$O)$_2$C$_6$H$_4$	**30a**·4C$_4$H$_8$O$_2$·2H$_2$O
formula	$C_{92}H_{132}B_{40}O_{10}$	$C_{107}H_{132}B_{40}O_{10}$	$C_{172}H_{236}B_{60}O_{16}$	$C_{107}H_{116}B_{40}N_4O_{17}$
M_r	1830.38	2010.53	3208.21	2162.44
T [K]	100(2)	293(2)	105(2)	293(2)
crystal system	triclinic	tetragonal	monoclinic	triclinic
space group	$P\bar{1}$	$I\bar{4}$	$P2_1/c$	$P\bar{1}$
a [Å]	11.643(5)	18.215(9)	15.088(1)	17.775(2)
b [Å]	14.614(7)	18.215(9)	33.929(3)	18.118(2)
c [Å]	16.493(8)	17.719(10)	18.498(2)	21.104(3)
α [°]	84.694(9)	90	90	103.588(2)
β [°]	76.814(8)	90	103.880(2)	103.881(2)
γ [°]	86.499(9)	90	90	96.716(2)
V [Å^3]	2718(2)	5879(5)	9193.1(1)	6304.2(13)
Z	1	2	2	2
ρ_{calcd} [g cm^{-3}]	1.118	1.136	1.159	1.139
μ [mm^{-1}]	0.064	0.490	0.066	0.070
F(000)	964	2108	3392	2244
crystal size [mm]	0.02 × 0.20 × 0.40	0.35 × 0.35 × 0.35	0.20 × 0.50 × 0.50	0.10 × 0.10 × 0.35
θ_{max} [°]	28.42	57.47	28.31	23.30
index ranges	−15/15, −17/19, −21/19	0/19, 0/19, 0/19	−20/19, −38/44, −23/24	−14/19, −20/17, −23/22
unique reflections	17720	2234	21917	17897
reflections observed [$I > 2\sigma(I)$]	3792	1258	8188	7703
parameters	444	340	1149	897
$R1$ [$I > 2\sigma(I)$]	0.1553	0.0776	0.0632	0.1631
$wR2$	0.4559	0.2543	0.1461	0.4767
largest diff. peak/hole [e Å^{-3}]	+0.686/−0.392	+0.188/−0.160	+0.298/−0.221	+1.249/−0.656

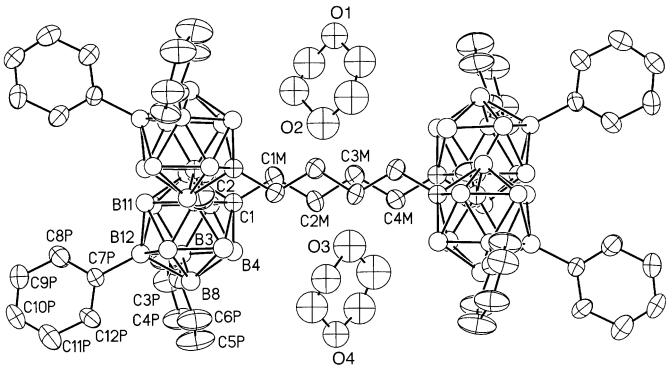


Figure 6. ORTEP representation showing the molecular structure of **28a**.

ably, two dioxane molecules are found in close proximity above and below the center of the cavity (Figure 6).

The molecular structure of **28b**, the first known hexameric carboracycle, is depicted in Figure 7. The centrosymmetric molecule crystallized in a pseudo-chair conformation together with eight solvent molecules of 1,3-dimethoxybenzene. Their closest contacts with **28b** all involve interactions of oxygen atoms to hydrogen atoms of B–H vertices, methylene moieties, and aryl carbon atoms of the cage-bound phenyl groups. The shortest interaction observed is a $CH_2\cdots O$ distance of 2.51 Å, within the range of van der Waals separations.[31] Comparable to the tetramer **28a**, the molecular structure of **28b** also shows 1,3-dimethoxybenzene molecules positioned above and below the center of the cavity.

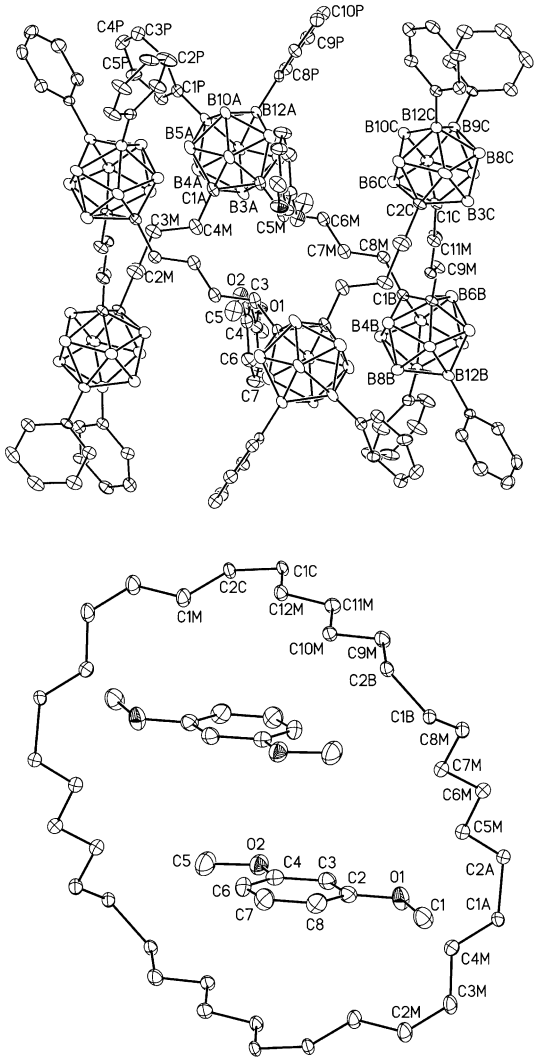
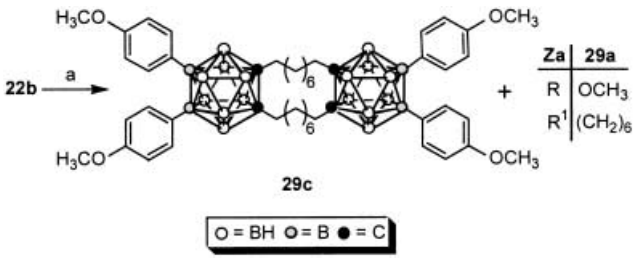


Figure 7. Top: ORTEP representation of hexameric octaphenyl cycle **28b**, sideview. The macrocycle describes the crownlike structure capturing two of the six 1,3-dimethoxybenzene molecules. Bottom: Top view of **28b**, cage-B vertices omitted for clarity; the representation displays the 32-membered ring of carbon atoms containing two solvent molecules.

The observation that, unlike compound **27a**, the cycles **28a** and **28b** display host–guest type chemistry suggested the synthesis of carboracycles with larger cavity sizes by deploying longer linker moieties. However, the reaction of **22b-Li$_2$** with one equivalent of 1,8-dibromooctane afforded cyclic tetramer **29a** in only 9% yield, while the principal product and cyclic dimer **29c** was formed in 71% yield (Scheme 3). It



Scheme 3. Dimeric carboracycle forms in 71% yield: a) 1. *n*BuLi, 2. $Br(CH_2)_8Br$.

is apparent that the longer the bridging hydrocarbon unit the more the formation of a dimeric cycle is favored. This observation is supported by the previous discovery that dimeric and tetrameric cycles form in a ratio of 1:2, respectively, upon linking 1,2-carborane via *m*-xylenylidene units.[13]

Previous attempts to assemble four 1,2-carborane cages in a cyclic manner via 2,6-lutidylidene tethers unexpectedly failed.[13] In revisiting this goal, the bis-lithiated tetraanisole derivative **24b** was treated with 1 molar equivalent of α,α'-dibromo-2,6-lutidine[32] to afford cyclic tetramer **30a** in low yield accompanied by starting material and unidentified material (Scheme 2). Compound **30a** was isolated by multiple fractional crystallizations in 10% yield. It was characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography (Table 2).

A suitable crystal for the X-ray diffraction study was grown from a solution of **30a** in dichloromethane/tetrahydrofuran. The molecular structure of **30a** (Figure 8) shows that two opposite pyridine rings are approximately parallel with a deviation of 21.3°. The distance between the centroids of these two rings is 3.77 Å, suggesting π-stacking involvement. The remaining two pyridine rings are tilted 69.3° with respect to each other and their centroids are separated by 9.43 Å.

Compound **30a** is potentially useful as a complexing reagent for metal ions. However, no evidence of Cu^{2+} complexation was found upon treatment of **30a** with copper(II) triflate. Futhermore, quarternization and protonation of the pyridyl nitrogen centers with methyl triflate and triflic

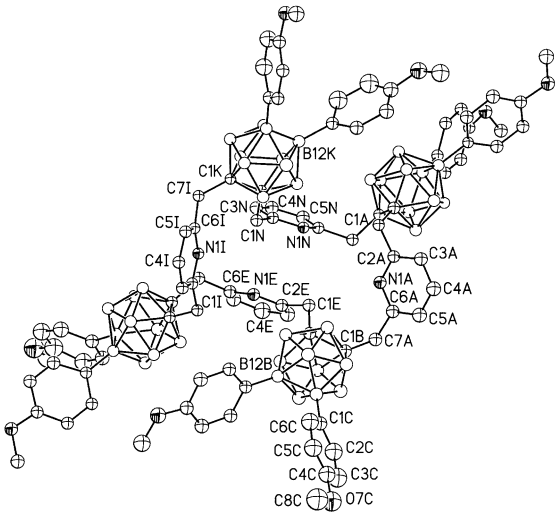


Figure 8. ORTEP representation showing the molecular structure of **30a**.

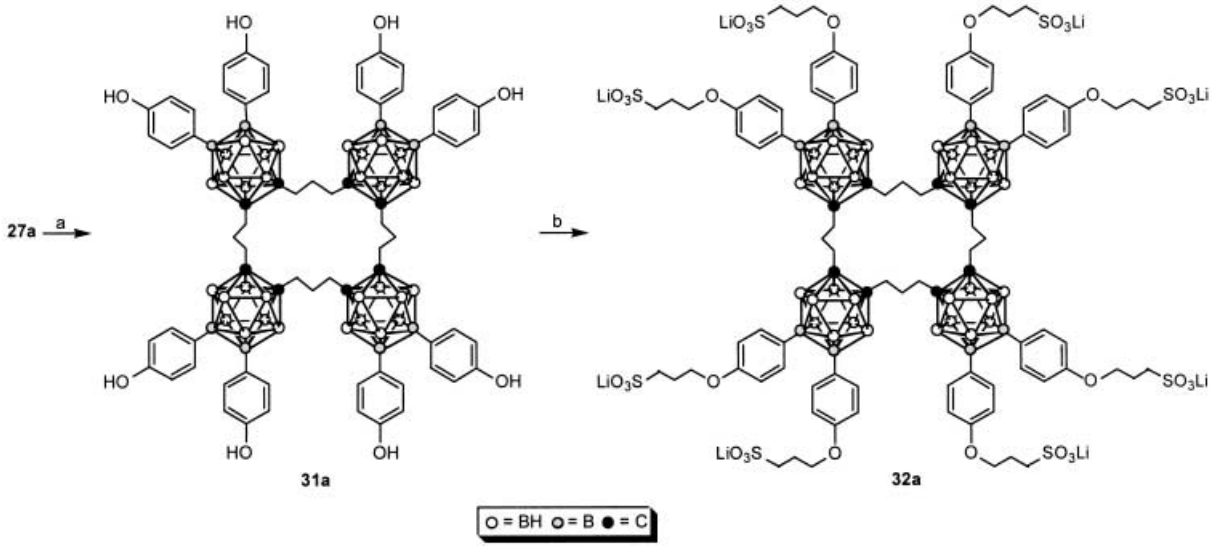
acid, respectively, did not take place. A comparably poor nucleophilicity of lutidylidene moieties connecting two carborane cages had been previously observed in a dimeric carboracycle containing 1,7-carborane.[13]

To transform the macrocycle **28a** into a water soluble species it was sulfonated at the phenyl residues using chlorosulfonic acid followed by hydrolysis. Electrophoresis and HPLC analysis of the water soluble product, however, proved it to be an inseparable mixture of regioisomers; furthermore, mass spectrometric analysis of the mixture indicated that more than eight sulfonate groups were attached to some cycles. Alternatively, the reaction of the cyclic tetramer **27a** with BBr_3 in dichloromethane provided the octa-4-hydroxyphenyl-substituted cycle **31a** in 80% yield (Scheme 4).[33] Both ^1H and ^{13}C NMR spectra confirmed the purity of **31a** by the absence of the signal for the protons of the remaining methoxy groups. Further reaction of **31a** with methyl sulfoxide methanide ($CH_3SOCH_2^-$) in DMSO, produced in situ from *n*-butyllithium and DMSO,[34] followed by treatment with 1,3-propane sultone generated the water-soluble octasulfonate **32a** through a ring-opening reaction. The product mixture was purified by HPLC to recover pure **32a-Li$_8$** in 35% yield.

Compound **32a** exhibits excellent water solubility, and, unlike sulfonated **28a**, particle size analysis for ultrasonicated aqueous solutions of **32a** gave rise to the formation of longer aggregates such as micelles. Further investigation of these properties are under way.

Conclusion

We have described the syntheses of both the 1,2- and 1,7-isomers of novel *para*-phenyl-substituted icosahedral *B*,*B*′-diaryl closo-carboranes by reacting the parent *B*,*B*′-diiodides with aryl Grignard reagents under Kumada coupling conditions. Furthermore selected bis(aryl)-1,2-carboranes were used as synthons in the formation of macrocycles with an organic linker. As demonstrated, the size and geometry of the cycles, the nature of the functional groups in the *para*-position of the phenyl substituents, as well as the nature of the linking moiety can be tuned in a controlled fashion to give a variety of novel structures. Interestingly, the formation of dimeric cycles is preferred with increasing chain length of the organic tether. However, butylidene-linked compound **28b** has been structurally identified and represents the first hexameric carboracycle to date. The observed molecular interaction in the crystal structures of tetrameric **28a** and **28b** between the cavity center and solvent molecules (dioxane in **28a** and 1,3-dimethoxybenzene in **28b**) suggests a basis for further exploration of carboracycles in host–guest chemistry. Moreover, compound **32a**, with eight sulfonate substituents, exemplifies the first water-soluble carboracycle. Alternatively, the attachment of long hydrocarbon chains at the hydroxyl groups of deprotected **30a** could lead to discotic liquid crystal carboracycles upon metal cation complexation.[35] The development of new supramolecular chemistry and its use in



Scheme 4. Synthesis of a water soluble carboracycle: a) BBr_3; b) 1. DMSO, *n*BuLi, 2. 1,3-trimethylene sultone.

molecular recognition in solvent systems that range from organic to aqueous represent future applications of these novel functionalizable carboracycles.

Experimental Section

General considerations: Standard Schlenk and vacuum line techniques were employed when appropriate. All solvents used were reagent grade. The solvents CH_2Cl_2, CH_3CN, and NEt_3 were distilled from calcium hydride prior to their use. THF was distilled from sodium benzophenone ketyl. Acetone (Fisher Scientific) was used without further purification. The reagents 4-bromoanisole, 4-bromothioanisole, 4-bromo-*N*,*N*-dimethylaniline, 4-bromophenylethyleneketal, acetic anhydride, 4-chlorophenylmagnesium bromide (Et_2O), phenylmagnesium bromide (THF), methylmagnesium bromide (THF), $[PdCl_2(PPh_3)_2]$, KO_2, $(CH_3)_3SiCl$, $(NH_4)_2[Ce(NO_2)_6]$, (Aldrich) were used as purchased. The reagents $Br(CH_2CH_2O)_3CH_3$,[23] and 4,4′-bis(iodomethyl)-1,1′-biphenyl[36] were prepared as previously described. Infrared spectra were recorded on a Nicolet 470 FTIR spectrophotometer. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AM400 and AM500 spectrometers. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to signals of residual ^1H and ^{13}C present in deuteriated solvents. Chemical shifts values for ^{11}B NMR spectra were referenced relative to external $BF_3 \cdot OEt_2$ ($\delta = 0.0$ ppm with negative values upfield). Mass spectra were obtained using a VG ZAB-SE (FAB), a VG Autospec (EI), and a Perkin Elmer Sciex API III triple quadrupole (ESI) mass spectrometer.

***closo*-9,12-(4-$CH_3OC_6H_4$)$_2$-1,2-$C_2B_{10}H_{10}$ (3)**: A solution of methyl magnesium bromide in THF (33 mL, 0.1 mol, 3 M) was added to a solution of *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (39.6 g, 0.1 mol) in THF (100 mL) at 0 °C. The reaction mixture was stirred for 3 h at ambient temperature. A freshly prepared Grignard solution of 4-bromoanisole (50 mL, 0.4 mol) in THF (300 mL) was added followed by the addition of a single portion of $[PdCl_2(PPh_3)_2]$ (2.1 g, 3.0 mmol). The reaction mixture was refluxed for 48 h, and upon completion of the reaction (^{11}B NMR) the solvent was removed under reduced pressure. The residue was treated with dilute HCl (5%, 300 mL) at 0 °C to destroy excess Grignard reagent. The aqueous mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were reduced in volume (100 mL) under reduced pressure, dried over magnesium sulfate, and filtered through Al_2O_3 using CH_2Cl_2. The solvent of the eluate was removed, and the resulting solid was recrystallized from acetone to yield **3** as colorless crystals (21.4 g, 60%). The supernant solution was dried and the residue was purified by chromatography on Al_2O_3 using CH_2Cl_2/hexanes to yield additional 7.1 g (20%) of **3**. M.p. 176–178 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.9-3.0$ (br, 8H; BH), 3.59 (s, 2H; CH), 3.73 (s, 6H; CH_3), 6.69 (d, $^3J(H,H) = 8.2$ Hz, 4H; C_6H_4), 7.14 (d, $^3J(H,H) = 8.2$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): $\delta =$ 50.0 ($C_{carboranyl}$), 54.1 (CH_3), 112.5, 133.7, 158.9 ppm (C_6H_4); $^{11}B\{^1H\}$ (160 MHz, $(CD_3)_2CO$): $\delta = -15.0$ (2B), -12.7 (4B), -8.4 (2B), 8.9 ppm (2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}{}^{16}O_2$: 356.2779; found: *m*/*z*: 356.2778 [M^+] ($\Delta = 0.1$ mmu); IR (KBr pellet): $\tilde{\nu} = 3069$, 3064 cm^{-1} (CH).

***closo*-9,10-(4-CH_3O-C_6H_4)$_2$-1,7-$C_2B_{10}H_{10}$ (8)**: Compound **8** was prepared in 78% yield by following the procedure described for the synthesis of **3**. M.p. 156–158 °C; ^1H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.2$ (br, 8H; BH), 3.67 (s, 2H; CH), 3.69 (s, 6H; CH_3), 6.70 (d, $^3J(H,H) = 8.2$ Hz, 4H; C_6H_4), 7.24 ppm (d, $^3J(H,H) = 8.2$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): $\delta = 52.6$ ($C_{carboranyl}$), 55.1 (CH_3), 113.8, 135.1, 160.2 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$): $\delta = -19.5$ (2B), -12.7 (4B), -7.0 (2B), 1.0 (2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}{}^{16}O_2$: 356.2779; found: *m*/*z*: 356.2780 [M^+] ($\Delta = 0.1$ mmu).

***closo*-9,12-(4-HOC_6H_4)$_2$-1,2-$C_2B_{10}H_{10}$ (12)**: A solution of BBr_3 in CH_2Cl_2 (1.12 mL, 1.12 mmol, 1 M) was added dropwise to a solution of compound **3** (0.500 g, 1.40 mmol) dissolved in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred for 12 h at ambient temperature. The reaction mixture was dried in vacuo and then quenched slowly using water (30 mL), while maintaining vigorous stirring. The aqueous phase was extracted with ethyl acetate and the organic layer was flashed through a bed of silica gel using ethyl acetate. The filtrate was freed of solvent and recrystallized from diethyl ether to yield **12** as a colorless solid (0.424 g, 94%). M.p. 224–226 °C; ^1H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 1.9-2.9$ (br, 8H; BH), 4.55 (s, 2H; CH), 6.56 (d, $^3J(H,H) = 8.1$ Hz, 4H; C_6H_4), 7.02 (d, $^3J(H,H) = 8.1$ Hz, 4H; C_6H_4), 7.96 ppm (s, 2H; OH); $^{13}C\{^1H\}$ NMR (126 MHz, $(CH_3)_2CO$): $\delta = 50.7$ ($C_{carboranyl}$), 114.9, 134.8, 157.4 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$): $\delta = -15.0$ (2B), -12.7 (4B), -8.4 (2B), 8.8 ppm (2B); HRMS (EI): calcd for $^{12}C_{14}{}^1H_{20}{}^{11}B_{10}{}^{16}O_2$: 328.2466; found: *m*/*z*: 328.2474 [M^+] ($\Delta = 0.8$ mmu); IR (KBr pellet): $\tilde{\nu} = 3064$ cm^{-1} (CH).

***closo*-9,10-(4-HOC_6H_4)$_2$-1,7-$C_2B_{10}H_{10}$ (13)**: Compound **13** was prepared by following the procedure described for the synthesis of **12** to yield 0.425 g (90%) as a colorless crystalline solid after recrystallization from diethyl ether. M.p. 193–195 °C; ^1H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.2$ (br, 8H; BH), 3.64 (s, 2H; CH), 6.61 (d, $^3J(H,H) = 8.4$ Hz, 4H; C_6H_4), 7.15 (d, $^3J(H,H) = 8.4$ Hz, 4H; C_6H_4), 8.05 ppm (s, 2H; OH); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): $\delta = 52.4$ ($C_{carboranyl}$), 115.2, 135.2, 157.7 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $(CD_3)_2CO$): $\delta = -19.4$ (2B), -12.6 (4B), -6.9 (2B), 1.3 ppm (2B); HRMS (EI): calcd for $^{12}C_{14}{}^1H_{20}{}^{11}B_{10}{}^{16}O_2$: 328.2466; found: *m*/*z*: 328.2465 [M^+] ($\Delta = 0.1$ mmu).

***closo*-9,12-(4-$CH_3(OCH_2CH_2)_3OC_6H_4$)$_2$-1,2-$C_2B_{10}H_{10}$ (14)**: A suspension of **12** (0.647 g, 1.97 mmol) and potassium carbonate (1.50 g, 10.86 mmol) in acetone (20 mL) was stirred for 1 h, and then $Br(CH_2CH_2O)_3CH_3$ (2.46 g 10.86 mmol) was added. The reaction mixture was then refluxed for 48 h. The solvent was removed under reduced pressure and the resulting residue was neutralized with aqueous HCl (10%). The aqueous layer was extracted with diethyl ether (8 × 50 mL). The combined organic phases were dried over anhydrous magnesium sulfate and filtered. After removal of the solvent, the remaining residue was purified by chromatography on silica gel with diethyl ether and pentane (3:1) to yield **14** as a clear liquid (0.909 g, 74.5%); ^1H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.9-2.9$ (br, 8H; BH), 3.26 (s, 6H; CH_3), 3.45, 3.56, 3.57, 3.61, 3.75, 4.02 (t, $^3J(H,H) = 6.0$ Hz, 4H; CH_2), 4.59 (s, 2H; CH), 6.67 (d, $^3J(H,H) = 8.3$ Hz, 4H; C_6H_4), 7.09 ppm (d, $^3J(H,H) = 8.3$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $(CH_3)_2CO$): $\delta =$ 51.1 ($C_{carboranyl}$), 58.9 (CH_3), 67.9, 70.3, 71.0, 71.2, 71.3, 72.6 (CH_2), 114.2, 134.7, 159.2 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = -15.5$ (2B), -13.0 (4B), -8.2 (2B), 9.4 (2B); MS (EI): calcd for $^{12}C_{28}{}^1H_{48}{}^{11}B_{10}{}^{16}O_8$: 620.4352; found: *m*/*z*: 620.4335 [M^+] ($\Delta = 1.7$ mmu).

***closo*-9,12-(C_6H_5)$_2$-1,2-$C_2B_{10}H_{10}$ (1)**: Compound **1** was prepared by following the procedure described for the synthesis of **3**, but omitting the preliminary deprotonation with MeMgBr and by using *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (7.33 g, 18.51 mmol), phenylmagnesium bromide (92.5 mL, 1 M in THF), and $[PdCl_2(PPh_3)_2]$ (0.52 g, 0.714 mmol). Subsequent extractions of the crude product, flash chromatography on Al_2O_3, as well as final recrystallization were performed with diethyl ether to afford **1** as an off-white solid (3.95 g, 72%). M.p. 288–289 °C; ^1H NMR (500 MHz, [D$_8$]THF): $\delta = 1.9-3.1$ (br, 8H; BH), 4.47 (s, 2H; CH), 6.99, 7.14 ppm (m, 10H; C_6H_5); $^{13}C\{^1H\}$ NMR (126 MHz, [D$_8$]THF): $\delta = 51.5$ ($C_{carboranyl}$), 127.5, 127.8, 133.8 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, [D$_8$]THF): $\delta =$ -16.4 (2B), -14.1 (4B), -9.6 (2B), 7.2 ppm (2B); HRMS (EI): calcd for $^{12}C_{14}{}^1H_{20}{}^{11}B_{10}$: 296.2550; found: *m*/*z*: 296.2566 [M^+] ($\Delta = 1.6$ mmu); IR (KBr pellet): $\tilde{\nu} = 3069$ cm^{-1} (CH).

***closo*-9,12-(4-$CH_3SC_6H_4$)$_2$-1,2-$C_2B_{10}H_{10}$ (4)**: Compound **4** was prepared by following the procedure described for the synthesis of **3** with *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (2.0 g, 5.0 mmol), methyl magnesium bromide (1.7 mL, 5.0 mmol, 3 M in THF), freshly prepared Grignard of 4-bromothioanisole (10.0 g, 49.2 mmol), and $[PdCl_2(PPh_3)_2]$ (0.142 g, 0.2 mmol). Subsequent extractions of the crude product and flash chromatography on silica gel were conducted with diethyl ether. Final purification was achieved by chromatography on silica gel with CH_2Cl_2 and hexanes (1:1). Recrystallization from the same solvent mixture provided **4** as colorless crystals (1.32 g, 73%); M.p. 193–195 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.8-3.1$ (br, 8H; BH), 2.42 (s, 6H; CH_3), 3.64 (s, 2H; CH), 7.02 (d, $^3J(H,H) =$ 8.2 Hz, 4H; C_6H_4), 7.13 ppm (d, $^3J(H,H) = 8.2$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 15.7$ (CH_3), 49.3 ($C_{carboranyl}$), 125.6, 133.5, 137 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = -14.9$ (2B), -12.7 (4B), -8.5 (2B), 8.3 (2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}{}^{32}S_2$: 388.2332; found: *m*/*z*: 388.2326 [M^+] ($\Delta = 0.6$ mmu).

***closo*-9,12-[4-$CH_3S(O)C_6H_4$)]$_2$-1,2-$C_2B_{10}H_{10}$ (15)**: A solution of CAN (2.93 g, 5.35 mmol) in water (20 mL) was added to a solution of bis-thioether **4** (0.50 g, 1.29 mmol) and $[(nBu)_4N]Br$ (33 mg, 0.10 mmol) in CH_2Cl_2 (50 mL) at room temperature, and the reaction mixture was stirred until the yellow color disappeared (6 to 8 h). The organic layer was

separated, and the aqueous layer was washed with CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried under reduced pressure. The solid residue was redissolved in Et_2O and washed thoroughly with water (4 × 25 mL). The ethereal phase was dried to yield **15** as a waxy solid (0.50 g, 92%). M.p. 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.7-3.2$ (br, 8H; BH), 2.56 (s, 6H; CH_3), 3.87 (s, 2H; $C_{carboranyl}$-H), 7.28 ppm (m, 8H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 43.6$ (CH_3), 50.7 ($C_{carboranyl}$), 122.4, 133.8, 144.0 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta = -13.8$ (br m, 6B), −8.6 (2B), 6.8 ppm (2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}{}^{32}S_2{}^{16}O_2$: 420.2230; found: *m/z*: 420.2228 [M^+] ($\Delta = 0.2$ mmu).

***closo*-9,12-[4-CH$_3$S(O)$_2$C$_6$H$_4$)]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (16)**: Reactions of **4** with two equivalents of *m*-chloroperbenzoic acid and manganese dioxide, respectively, carried out in accordance with published procedures,[25] generated mixtures of **15** and **16**. Pure **16** was obtained by chromatography on silica (hexanes/ethyl acetate 1:1) in 10 and 20% yield, respectively. M.p. 252 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.7-3.2$ (br, 8H; BH), 2.97 (s, 6H; CH_3), 3.81 (s, 2H; $C_{carboranyl}$-H), 7.37 (d, ^3J(H,H) = 7.9 Hz, 4H; C_6H_4), 7.66 ppm (d, ^3J(H,H) = 7.9 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 44.6$ (CH_3), 51.0 ($C_{carboranyl}$), 126.2, 133.8, 139.8 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta = -15.6$ (br, 2B), −13.7 (br, 4B), −9.2 (s, 2B), 7.0 ppm (s, 2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}{}^{32}S_2{}^{16}O_4$: 453.2098; found: *m/z*: 453.2095 [M^+] ($\Delta = 0.3$ mmu).

***closo*-9,12-(4-(CH$_3$)$_2$NC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (5)**: Compound **5** was prepared following the procedure described for the synthesis of **3** by using *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (11.0 g, 27.8 mmol), methyl magnesium bromide (9.2 mL, 27.9 mmol, 3 M in THF), freshly prepared Grignard of 4-bromo-*N*,*N*-dimethylaniline (25.0 g, 124.9 mmol), and [$PdCl_2(PPh_3)_2$] (0.11 g, 0.156 mmol). Subsequent extractions of the crude product, flash chromatography on Al_2O_3, as well as final recrystallization were performed with ethyl acetate to afford **5** as an off white solid (8.09 g 76%). M.p. 280 °C (decomp); ^{1}H NMR (500 MHz, CD_3OD): $\delta = 1.8-3.1$ (br, 8H; BH), 4.71 (s, 2H; CH), 4.85 (s, 12H; CH_3), 7.40 ppm (m, 8H; C_6H_4); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD): $\delta = 47.4$ (CH_3), 53.6 ($C_{carboranyl}$), 120.4, 136.0, 143.2 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, CD_3OD): $\delta = -13.4$ (br, 6B), −9.4 (2B), 6.4 ppm (2B); HRMS (EI): calcd for $^{12}C_{18}{}^1H_{30}{}^{11}B_{10}{}^{14}N_2$: 382.3421; found: *m/z*: 382.3415 [M^+] ($\Delta = 0.6$ mmu).

***closo*-9,10-(4-(CH$_3$)$_2$NC$_6$H$_4$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (9)**: Compound **9** was prepared and purified by following the procedure described for the synthesis of **5** to afford colorless crystals (82%). M.p. 195–196 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.1$ (br, 8H; BH), 2.84 (s, 12H; CH_3), 3.58 (s, 2H; CH), 6.83 ppm (m, 8H; C_6H_4); ^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): $\delta =$ 40.4 (CH_3), 51.9 ($C_{carboranyl}$), 112.7, 134.8, 150.9 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CD_3)_2CO$): $\delta = -19.5$ (2B), −12.4 (4B), −6.7 (2B), 1.8 ppm (2B); HRMS (FAB, positive mode): calcd for $^{12}C_{18}{}^1H_{30}{}^{11}B_{10}{}^{14}N_2$: 382.3421; found: *m/z*: 382.3421 [M^+] ($\Delta = 0.0$ mmu).

***closo*-9,12-(4-ClC$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (6)**: Compound **6** was prepared by following the procedure described for the synthesis of **3** with *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (0.20 g, 0.51 mmol), methyl magnesium bromide (0.17 mL, 0.51 mmol, 3 M in THF), 4-chloro-phenylmagnesium bromide (4.0 mL, 1 M in diethyl ether), and [$PdCl_2(PPh_3)_2$] (0.01 g, 0.014 mmol). After standard workup, the crude product was flashed through a bed of basic aluminum oxide, with toluene as the eluting solvent, followed by silica gel chromatography, with pentane and diethyl ether (5:1) eluting solvent, to yield **6** as a colorless solid (0.146 g, 81%). M.p. 140–143 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.1$ (br, 8H; BH), 4.74 (s, 2H; CH), 7.1 ppm (m, 8H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 49.7$ ($C_{carboranyl}$), 127.7, 133.7, 134.3 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): $\delta = -16.8$ (2B), −14.4 (4B), −9.7 (2B), 6.8 ppm (2B); HRMS (FAB, positive mode): calcd for $^{12}C_{14}{}^1H_{18}{}^{11}B_{10}{}^{35}Cl_2$: 365.1752; found: *m/z*: 365.1760 [M^+] ($\Delta = 0.8$ mmu); IR (KBr pellet): $\tilde{\nu} = 3067$ (CH), 2820 cm^{-1} (BH).

***closo*-9,10-(4-ClC$_6$H$_4$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (10)**: Compound **10** was prepared and purified by following the procedure described for the synthesis of **6** to yield **10** as a white solid (yield 88%). M.p. 152–153 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.1$ (br, 8H; BH), 3.82 (s, 2H; CH), 7.2 ppm (m, 8H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): $\delta = 53.4$ ($C_{carboranyl}$), 128.3, 134.1, 135.5 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, THF): $\delta = -18.5$ (2B), −12.2 (4B), −6.5 (2B), 0.8 ppm (2B); HRMS (FAB, positive mode): calcd for $^{12}C_{14}{}^1H_{18}{}^{11}B_{10}{}^{35}Cl_2$: 365.1752; found: *m/z*: 365.1765 [M^+] ($\Delta = 1.3$ mmu).

***closo*-9,12-(4-CH$_3$C$_6$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (2)**: Compound **2** was prepared by following the procedure described for the synthesis of **3**, but omitting the preliminary deprotonation, with MeMgBr *Closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (7.33 g, 18.51 mmol), tolylmagnesium bromide (92.5 mL, 1 M in THF), and [$PdCl_2(PPh_3)_2$] (0.519 g, 0.714 mmol). Subsequent extractions of the crude product, flash chromatography on Al_2O_3, as well as final recrystallization from a toluene/pentane mixture afforded **2** as colorless crystals (4.56 g, 76%). M.p. 280 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.8-3.1$ (br, 8H; BH), 2.17 (s, 6H; CH_3), 4.62 (s, 2H; CH), 6.88 (d, ^3J(H,H) = 7.8 Hz, 4H; C_6H_4), 7.09 ppm (d, ^3J(H,H) = 7.8 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): $\delta = 21.1$ (CH_3), 51.4 ($C_{carboranyl}$), 128.7, 133.6, 36.9 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CD_3)_2CO$): $\delta = -15.2$ (2B), −12.6 (4B), −8.0 (2B), 9.2 (2B); HRMS (EI): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}$: 324.2889; found: *m/z*: 324.2888 [M^+] ($\Delta = 0.1$ mmu).

***closo*-9,10-(4-CH$_3$C$_6$H$_4$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (7)**: Compound **7** was prepared and purified by following the procedure described for the synthesis of **2** to afford colorless crystals (25 mg, 78%). M.p. 158 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.9-3.2$ (br, 8H; BH), 2.19 (s, 6H; CH_3), 3.70 (s, 2H; CH), 6.93 (d, ^3J(H,H) = 7.9 Hz, 4H; C_6H_4), 7.23 ppm (d, ^3J(H,H) = 7.9 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): $\delta = 21.1$ (CH_3), 52.8 ($C_{carboranyl}$), 128.9, 113.9, 137.2 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CD_3)_2CO$): $\delta = -19.1$ (2B), −12.2 (4B), −6.4 (2B), 1.8 ppm (2B); HRMS (FAB, positive mode): calcd for $^{12}C_{16}{}^1H_{24}{}^{11}B_{10}$: 324.2881; found: *m/z*: 324.2865 [M^+] ($\Delta = 1.6$ mmu).

***closo*-9,10-(4-CH$_3$C[(OCH$_2$)$_2$]C$_6$H$_4$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (11)**: Compound **11** was prepared by following the procedure described for the synthesis of **3** with *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ (200 mg, 0.50 mmol), methyl magnesium bromide (0.17 mL, 0.50 mmol, 3 M in THF), freshly prepared Grignard of 4-bromoacetophenone ethylene ketal (1.12 g, 4.61 mmol),[14] and [$PdCl_2(PPh_3)_2$] (10 mg, 0.014 mmol). The reaction mixture was quenched with aqueous $NaHCO_3$ solution. The organic phase was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic phase was dried over magnesium sulfate and filtered. The solvent was removed, and the residue was filtered through a bed of basic Al_2O_3 with toluene as the eluting solvent and subsequently purified by chromatography on basic Al_2O_3 with pentane and diethyl ether (4:1) to yield **11** as a white solid (150 mg, 63%). M.p. 148–150 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.48$ (s, 6H; CH_3), 1.9–3.2 (br, 8H; BH), 3.65 (m, 4H; CH_2), 3.78 (s, 2H; CH), 3.94 (m, 4H; CH_2), 7.21 (d, ^3J(H,H) = 8.0 Hz, 4H; C_6H_4), 7.32 ppm (d, ^3J(H,H) = 8.0 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): $\delta = 27.8$ (CH_3), 53.2 ($C_{carboranyl}$), 64.9 (CH_2), 109.2 (OCO), 125.0, 133.8, 143.4 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CD_3)_2CO$): $\delta = -19.3$ (2B), −12.9 (4B), −7.2 (2B), 0.4 (2B); HRMS (EI): calcd for $^{12}C_{22}{}^1H_{32}{}^{11}B_{10}{}^{16}O_4$: 468.3315; found: *m/z*: 468.3257 [M^+] ($\Delta =$ 5.8 mmu).

***closo*-9,10-(4-CH$_3$CO-C$_6$H$_4$)$_2$-1,7-C$_2$B$_{10}$H$_{10}$ (18)**: 20% HCl (10 mL) was added to a solution of **11** (100 mg, 0.213 mmol) in THF (20 mL), and the mixture was stirred at ambient temperature for 4 h. Water (20 mL) and diethyl ether (20 mL) were added with stirring. The organic phase was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over magnesium sulfate and filtered. The solvent was removed, and the resulting residue was triturated with diethyl ether to give **18** as a white solid (72 mg, 89%). M.p. 176 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.9-3.2$ (br, 8H; BH), 2.48 (s, 6H; CH_3), 3.89 (s, 2H; CH), 7.48 (d, ^3J(H,H) = 8.2 Hz, 4H; C_6H_4), 7.74 ppm (d, ^3J(H,H) = 8.2 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): $\delta = 25.7$ (CH_3), 52.8 ($C_{carboranyl}$), 127.1, 133.2, 136.2 (C_6H_4), 196.9 ppm (CO); ^{11}B{^{1}H} NMR (160 MHz, $(CD_3)_2CO$): $\delta = -17.7$ (2B), −11.6 (4B), −6.2 (2B), 1.1 ppm (2B); HRMS (EI): calcd for $^{12}C_{18}{}^1H_{24}{}^{11}B_{10}{}^{16}O_2$: 380.2789: found: *m/z*: 380.2784 [M^+] ($\Delta = 0.5$ mmu); IR (KBr pellet) $\tilde{\nu} = 3064$ (CH), 1688, 1675 cm^{-1} (C=O).

***closo*-9,10-(4-CH$_3$COOC$_6$H$_4$)2-1,7-C$_2$B$_{10}$H$_{10}$ (17)**: Neat acetic anhydride (0.10 mL, 1.08 mmol) was added to a suspension of **13** (52 mg, 0.158 mmol) in THF (30 mL) and NEt_3 (0.21 mL, 1.50 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature, and afterwards all volatiles were removed in vacuo. The resulting residue was redissolved in CH_2Cl_2. The organic layer was washed three times with water and dried, and the residue was recrystallized from diethyl ether to yield **17** as a white solid (48 mg, 74%). M.p. 273–275 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.9-3.2$ (br, 8H; BH), 2.24 (s, 6H; CH_3), 3.65 (s, 2H; CH), 6.83 (d, ^3J(H,H) = 8.4 Hz, 4H; C_6H_4), 7.19 ppm (d, ^3J(H,H) = 8.4 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): $\delta = 21.2$ (CH_3), 49.3 ($C_{carboranyl}$), 129.2, 133.9, 150.1 (C_6H_4), 169.5 ppm (CO); ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -16.2$ (2B), -13.9 (4B), -9.2 (2B), 7.4 ppm (2B); HRMS (EI): calcd for $^{12}C_{18}{}^{1}H_{24}{}^{11}B_{10}{}^{16}O_4$: 412.2687; found: m/z: 412.2694 [M^+] ($\Delta = 0.7$ mmu).

1-(*tert*-Butyldimethylsilyl)-9,12-di(4-methoxyphenyl)-1,2-carborane (19): *n*-Butyllithium (6.8 mL, 16.44 mmol, 2.5 M in hexane) was added dropwise to a solution of **3** (5.86 g, 16.44 mmol) in THF (100 mL) at 0 °C. After stirring for 4 h at room temperature *tert*-butyldimethylsilyl chloride (2.97 g, 19.73 mmol) was added, and the reaction mixture was stirred for a further 8 h. The solution was quenched with brine and extracted with diethyl ether (3×50 mL). The combined organic layers were dried over magnesium sulfate, the solvent was removed under vacuum, and the residue was subjected to flash silica gel chromatography with CH_2Cl_2 and pentane (1:1) as the eluting solvent to yield **19** (7.54 g, 97.5 %) as a waxy white solid. M.p. 131–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 6H; $SiCH_3$), 1.06 (s, 9H; CCH_3), 1.9–3.0 (br, 8H; BH), 3.52 (s, 1H; CH), 3.73, 3.74 (s, 3H; OCH_3), 6.68, 6.69 (d, ^3J(H,H) = 8.6 Hz, 2H; C_6H_4), 7.13, 7.16 ppm (d, ^3J(H,H) = 8.6 Hz, 2H; C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = -4.4$ ($SiCH_3$), 19.4 (SiC), 27.0 (CCH_3), 54.6 ($CC_{carboranyl}$), 54.9 (CH_3), 58.6 ($SiC_{carboranyl}$), 112.8, 133.8, 133.9, 158.8 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta = -13.1$ (2B), -10.5 (2B), -9.5 (2B), -5.8 (2B), 9.9 (1B), 11.9 ppm (1B), HRMS (EI): calcd for $^{12}C_{22}{}^{1}H_{38}{}^{11}B_{10}{}^{16}O_2{}^{28}Si$: 470.3657; found: m/z: 470.3640 [M^+] ($\Delta = 1.7$ mmu).

1,3-Bis(2′-(*tert*-butyldimethylsilyl)-9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)propane (20a): *n*-Butyllithium (6.08 mL, 15.21 mmol, 2.5 M in hexane) was added dropwise to a solution of **19** (7.17 g, 15.21 mmol) in THF (100 mL) at 0 °C. After stirring for 4 h at room temperature 1,3-dibromopropane (0.78 mL, 7.68 mmol) was added. The reaction mixture was refluxed for 12 h and washed with brine, and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic layers were dried over magnesium sulfate, the solvent was removed under vacuum, and the residue was subjected to flash silica gel chromatography with CH_2Cl_2/pentane (3:1) as the eluting solvent to yield **20a** (4.32 g, 57.8 %) as a waxy white solid and starting material (2.27 g, 4.81 mmol). Compound **20a** was recovered in an adjusted 84.4 % yield. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta =$ 0.42 (s, 12H; $SiCH_3$), 1.12 (s, 18H; CCH_3), 1.9–3.0 (br, 16H; BH), 1.97 (m, 2H; CH_2), 2.53 (t, ^3J(H,H) = 8.2 Hz, 4H; CCH_2), 3.67, 3.68 (s, 6H; CH_3), 6.64, 6.66 (d, ^3J(H,H) = 8.6 Hz, 4H; C_6H_4), 7.10, 7.11 ppm (d, ^3J(H,H) = 8.6 Hz, 4H; C_6H_4); ^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): $\delta = -1.6$ ($SiCH_3$), 21.6 (SiC), 28.5 (CCH_3), 32.8 (CH_2), 37.1 (CCH_2), 55.66, 55.68 (CH_3), 70.2 ($SiC_{carboranyl}$), 76.9 ($CC_{carboranyl}$), 114.15, 114.2, 135.1, 135.4, 160.5, 160.6 ppm (C_6H_4); ^{11}B NMR (160 MHz, $(CH_3)_2CO$): $\delta = -9.3$ (12B), -6.6 (4B), 7.9 (2B), 11.5 ppm (2B); MS (negative ion FAB): calcd for $C_{47}H_{80}B_{20}O_4Si_2$: 981.49; found: m/z: 980.84 [$M - H^+$].

1,3-Bis(9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)propane (20b): Compound **20a** (3.54 g, 3.61 mmol) was dissolved in THF (50 mL) and cooled to -78 °C. A 1.0 M solution of tetrabutylammonium fluoride (7.57 mL, 7.57 mmol) was added dropwise, and the reaction mixture was warmed to room temperature over 30 min. Brine (50 mL) and diethyl ether (30 mL) were added; the aqueous layer was separated and washed with diethyl ether (2×50 mL). Then the combined organic layers were dried over magnesium sulfate, and the solvent was removed. The residue was subjected to flash silica gel chromatography with CH_2Cl_2/pentane (3:1) as the eluting solvent to yield **20b** (2.17 g, 80.1 %) as a white solid. M.p. 106–109 °C; ^{1}H (500 MHz, $(CD_3)_2CO$): $\delta = 1.90$ (m, 2H; CH_3), 1.9–2.9 (br, 16H; BH), 2.54 (t, 4H; ^3J(H,H) = 8.5 Hz, CCH_2), 3.67, 3.68 (s, 6H; CH_3), 4.76 (s, 2H; CH), 6.64, 6.66 (d, 4H; ^3J(H,H) = 8.7 Hz, C_6H_4) 7.07, 7.10 ppm (d, 4H; ^3J(H,H) = 8.7 Hz, C_6H_4); ^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): $\delta =$ 29.4 (CH_2), 36.4 (CCH_2), 55.1 (CH_3), 55.9 ($HC_{carboranyl}$), 68.2 ($CC_{carboranyl}$), 113.0, 113.1, 134.1, 134.3, 159.1, 159.2 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta = -13.2$ (12B), -9.2 (4B), 5.2 (2B), 8.0 ppm (2B); HRMS (EI): calcd for $^{12}C_{35}{}^{1}H_{52}{}^{11}B_{20}{}^{16}O_4$: 753.5863; found: m/z: 753.5876 [M^+] ($\Delta =$ 1.3 mmu).

Synthesis of cyclic tetramer 27a and cyclic hexamer 27b: *n*-Butyllithium (2.65 mL, 6.64 mmol, 2.5 M in hexane) was added dropwise to a solution of **20b** (2.38 g, 3.16 mmol) in THF (50 mL) at 0 °C. After stirring for 4 h, 1,3-dibromopropane (0.32 mL, 3.16 mmol) was added, and the solution was refluxed for 12 h. The solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL) and the combined organic phase was washed with water and dried over magnesium sulfate. Removal of the solvent afforded a slightly yellow solid, which was purified by crystallization from acetone yielding **27a** (1.73 g, 69 %) and traces of the cyclic hexamer **27b**.

27a: M.p. >300 °C; ^{1}H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 1.92$ (br, 8H; CH_2), 2.0–2.9 (br, 32H; BH), 2.60 (br, 16H; CCH_2), 3.67 (s, 24H; CH_3), 6.63 (d, ^3J(H,H) = 8.7 Hz, 16H; C_6H_4), 7.07 ppm (d, ^3J(H,H) = 8.7 Hz, 16H; C_6H_4); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): $\delta = 31.7$ (CH_2), 33.8 (CCH_2), 55.2 (CH_3), 74.1 ($C_{carboranyl}$), 113.7, 134.9, 160.1 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz $(CH_3)_2CO$): $\delta = -9.7$ (32B), 7.2 ppm (8B); MS (positive ion FAB): calcd for $C_{114}H_{168}B_{60}O_{12}$: 1586.1; found: m/z: 1586.4 [M^+].

27b: MS (positive ion FAB): calcd for $C_{114}H_{168}B_{60}O_{12}$: 2379.8; found: m/z: 2379.81 [M^+].

Synthesis of octahydroxy cyclic tetramer 31a: BBr_3 (17.55 mL, 17.55 mmol, 1 M in CH_2C1_2) was added dropwise to a solution of **27a** (1.16 g, 0.73 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After stirring for 12 h the solvent was removed, the residue was quenched slowly with water (10 mL), and the mixture was stirred vigorously for 20 min. The resulting solid was then filtered, washed with water (3×15 mL), and finally crystallized from acetone to yield **31a** (0.86 g, 80 %) as a colorless crystalline solid. M.p. >300 °C; ^{1}H (500 MHz, $(CD_3)_2CO$): $\delta = 1.91$(br, 8H; CH_2), 1.9–2.9 (br, 32H; BH), 2.53 (br, 16H; CCH_2), 6.56 (d, ^3J(H,H) = 8.4 Hz, 16H; C_6H_4), 7.00 (d, ^3J(H,H) = 8.4 Hz, 16H; C_6H_4), 8.15 ppm (s, 8H; OH); ^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): $\delta = 31.9$ (CH_2), 33.8 (CCH_2), 74.2 ($C_{carboranyl}$), 115.0, 134.9, 157.4 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta = -9.0$ (32B), 8.0 ppm (8B); MS (positive ion FAB): calcd for $C_{68}H_{96}B_{40}O_8$: 1474.1; found: m/z: 1473.9 [M^+],.

Synthesis of water-soluble cyclic tetramer 32a: *n*-Butyllithium (0.337 mL, 0.842 mmol, 2.5 M in hexane) was added dropwise to a solution of **31a** (0.146 g, 0.099 mmol) in DMSO (20 mL) at 0 °C. After stirring this mixture for 12 h, 1,3-sultone (0.074 mL, 0.842 mmol) was added, and the mixture was stirred for an additional 2 days. The solvent was then removed, and the residue was triturated with acetone to give a yellowish solid, which was subjected to RP-HPLC (Beckman System Gold, 168 detector, 126 pump; C18-Dynamax-150a) under a H_2O/CH_3CN solvent gradient to recover **32a** (0.091 g, 37 %) as a white solid. M.p. >300 °C; ^{1}H NMR (500 MHz, CD_3OD): $\delta = 1.8$ (br, 8H; CH_2), 1.9–2.9 (br, 32H; BH), 2.18 (m, 16H; $CH_2CH_2SO_3Li$), 2.4 (br, 16H; CCH_2), 2.94 (t, ^3J(H,H) = 7.7 Hz, 16H; CH_2SO_3Li), 4.01 (t, ^3J(H,H) = 6.2 Hz, 16H; $CH_2CH_2CH_2SO_3Li$), 6.64, 7.05 ppm (d, ^3J(H,H) = 8.4 Hz, 16H; C_6H_4); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD): $\delta = 26.5$ ($CH_2CH_2SO_3Li$), 32.3 (CH_2), 34.1 (CCH_2), 62.0 (CH_2SO_3Li), 67.5 ($OCH_2CH_2CH_2SO_3Li$), 74.4 ($C_{carboranyl}$), 114.6, 135.4, 159.8 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, D_2O): $\delta = -10.3$ (32B), 6.1 ppm (8B). MS (negative mode electrospray, CH_3CN/H_2O 1:1): calcd for $C_{92}H_{144}B_{40}O_{22}S_8$:[37] 611.8, 815.8; found: m/z: 611.9 [M+4H]$^{4-}$, 815.9 [M+3H$^+$]$^{5-}$.

1-(*tert*-butyldimethylsilyl)-9,12-diphenyl-1,2-carborane (25): Compound **25** was prepared by following the procedure described for the synthesis of **19** to yield 6.79 g (98 %) as a waxy white solid. ^{1}H (400 MHz, $CDCl_3$): $\delta = 0.33$ (s, 6H; $SiCH_3$), 1.11 (s, 9H; CCH_3), 1.9–3.2 (br, 8H; BH), 3.58 (s, 1H; CH), 7.17 (m, 6H; C_6H_5), 7.29 ppm (m, 4H; C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): $\delta = -4.4$ ($SiCH_3$), 19.3 (SiC), 27.0 (CCH_3), 55.2 ($HC_{carboranyl}$), 59.3 ($SiC_{carboranyl}$), 126.81, 126.84, 127.1, 132.7, 132.8 ppm (C_6H_5); ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): $\delta = -14.6$ (2B), -12.3 (2B), -10.7 (2B), -6.8 (2B), 8.6 (1B), 10.5 ppm (1B); HRMS (EI): calcd for $^{12}C_{20}{}^{1}H_{34}{}^{11}B_{10}{}^{28}Si$: 410.3444; found: m/z: 410.3447 [M^+] ($\Delta = 0.3$ mmu).

1,4-Bis(2′-[*tert*-butyldimethylsilyl]-9′,12′-diphenyl-1′,2′-carboranyl)butane (26a): Compound **26a** was prepared by following the procedure described for the synthesis of **20a** to yield 5.71 g (82 %) as a waxy white solid. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 0.44$ (s, 12H; $SiCH_3$), 1.13 (s, 18H; CCH_3), 1.9–3.0 (br, 16H; BH), 1.69 (m, 4H; CH_2), 2.51 (m, 4H; CCH_2), 7.04–7.08 (m, 12H; C_6H_5), 7.19 ppm (m, 6H; C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): $\delta = 2.2$ ($SiCH_3$), 21.0 (SiC), 27.9 (CCH_3), 30.8 (CH_2), 37.3 (CCH_2), 70.7 ($SiC_{carboranyl}$), 77.7 ($CC_{carboranyl}$), 127.5, 127.6, 127.8, 127.9, 133.4, 133.7 ppm (C_6H_4); ^{11}B{^{1}H} NMR (160 MHz, $(CH_3)_2CO$): $\delta =$ (10.1 (12B), 7.2 (4B), 6.8 (2B), 10.3 ppm (2B); HRMS (negative ion FAB): calcd for $^{12}C_{44}{}^{1}H_{74}{}^{11}B_{20}{}^{28}Si_2$: 875.7335; found: m/z: 875.7330 [M^+], ($\Delta = 0.5$ mmu).

1,4-Bis(9′,12′-diphenyl-1′,2′-carboranyl)butane (26b): Compound **26b** was prepared by following the procedure described for the synthesis of **20b** to yield 3.34 g (98 %) as a waxy white solid. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): $\delta = 1.65$ (m, 4H; CH_2), 1.9–3.0 (br, 16H; BH), 2.51 (m, 4H; CCH_2), 7.05

(m, 6H; C_6H_5), 7.16 ppm (m, 4H; C_6H_5); $^{13}C\{^1H\}$ NMR (126 MHz, $(CD_3)_2CO$): $\delta = 29.8$ (CH_2), 37.3 (CCH_2), 57.9 ($HC_{carboranyl}$), 71.2 ($CC_{carboranyl}$), *127.47, 127.50, 127.7, 133.6, 133.9 ppm (C_6H_5); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$):* $\delta = -12.3$ (8B), -10.7 (4B), -8.6 (4B), 5.7 (2B), 8.5 ppm (2B); HRMS (EI): calcd for $^{12}C_{32}{}^1H_{46}{}^{11}B_{20}$: 647.5594; found: m/z: 647.5576 [M^+] ($\Delta = 1.8$ mmu).

Synthesis of cyclic tetramer 28a and cyclic hexamer 28b: *n*-Butyllithium (3.09 mL, 7.72 mmol, 2.5 M in hexane was added dropwise to a solution of **26b** (2.38 g, 3.67 mmol) in THF (50 mL) at 0 °C. After stirring for 4 h at room temperature, 1,4-dibromobutane (0.44 mL, 3.67 mmol) was added, and the solution was refluxed for 2 days. The reaction mixture was then washed with brine, the aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under vacuum providing a slightly yellow solid which was recrystallized in acetone to give 2.03 g (79 %) of crystalline **28a** and traces of **28b**.

28a: M.p. > 300 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.92$ (m, 8H; CH_2), 2.0–2.9 (br, 32H; BH), 2.24 (br, t, $^3J(H,H) = 8.7$ Hz, 16H; CCH_2), 3.67 (s, 24H; CH_3), 7.12 (m, 24H; C_6H_4), 7.20 ppm (m, 16H; C_6H_4); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.3$ (CH_2), 34.2 (CCH_2), 72.2 ($C_{carboranyl}$), 127.4, 127.5, 133.1 ppm (C_6H_5); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = -10.5$ (32B), 6.4 ppm (8B); MS (positive ion FAB): calcd for $C_{72}H_{104}B_{40}$: 1402.1; found: m/z: 1403.1 [M^++H].

28b: MS (positive ion FAB): calcd for $C_{108}H_{156}B_{60}$: 2103.1; found: m/z: 2104.1 [M^++H],.

1,6-Bis(2′-(*tert*-butyldimethylsilyl)-9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)hexane (21a): *n*-Butyllithium (0.92 mL, 2.29 mmol, 2.5 M in hexane) was added dropwise to a solution of **19** (1.03 g, 2.18 mmol) in THF (100 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 4 h, after which 1,6-dibromohexane (0.18 mL, 1.13 mmol) was added. After refluxing for 8 h, the solution was washed with brine, the aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were dried over magnesium sulfate. The solvent was removed under vacuum and the residue was subjected to flash silica gel chromatography with CH_2Cl_2/pentane (3:1) as the eluting solvent to yield **21a** as a white solid (0.91 g, 81 %). M.p. 218–220 °C; ^1H NMR (500 MHz, $(CDCl_3)$): $\delta = 0.36$ (s, 12H; $SiCH_3$), 1.09 (s, 18H; CCH_3), 1.25 (br, 4H; CH_2), 1.55 (br, 4H; CH_2), 2.26 (t, $^3J(H,H) = 8.4$ Hz, 4H; CCH_2), 1.9–3.0 (br, 16H; BH), 3.72, 3.73 (s, 3H; CH_3), 6.67, 6.68 (d, 4H; $^3J(H,H) = 8.7$ Hz, C_6H_4), 7.13, 7.14 ppm (d, 4H; $^3J(H,H) = 8.7$ Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = -2.1$ ($SiCH_3$), 20.6 (SiC), 27.8 (CCH_3), 29.3, 30.5 (CH_2), 37.2 (CCH_2), 55.1, 55.12 (CH_3), 68.7($SiC_{carboranyl}$), 75.7 ($CC_{carboranyl}$), 113.01, 113.02, 133.9, 134.3, 158.9, 159.0 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -10.2$ (12B), -7.2 (4B), 6.7 (2B), 10.3 (2B); MS (positive ion FAB): calcd for $C_{50}H_{86}B_{20}O_4Si_2$ 1023.6; found: m/z: 1024.0 [M^+].

1,6-Bis(9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)hexane (21b): Compound **21b** was prepared by following the procedure described for the synthesis of **20b** to yield 0.26 g (90 %) as a white solid. ^1H (500 MHz, $CDCl_3$): $\delta = 1.29$ (m, 4H; CH_2), 1.52 (m, 4H; CH_2), 2.28 (t, $^3J(H,H) = 8.6$ Hz, 4H; CCH_2), 1.9–3.0 (br, 16H; BH), 3.60 (s, 2H; CH), 3.72, 3.73 (s, 3H; CH_3), 6.67, 6.69 (d, $^3J(H,H) = 8.7$ Hz, 4H; C_6H_4), 7.12, 7.14 ppm (d, $^3J(H,H) = 8.7$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 28.8$, 29.5 (CH_2), 37.5 (CCH_2), 55.12, 55.13 (CH_3), 55.8 ($HC_{carboranyl}$), 69.5 ($CC_{carboranyl}$), 113.07, 113.08, 134.17, 134.39, 159.10, 159.12 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -12.9$ (12B), -9.0 (4B), 5.2 (2B), 8.1 ppm (2B); HRMS (EI): calcd for $^{12}C_{38}{}^1H_{58}{}^{11}B_{20}{}^{16}O_4$: 795.6335; found: m/z: 795.6331 [M^+] ($\Delta = 0.4$ mmu).

1,8-Bis(2′-(*tert*-butyldimethylsilyl)-9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)octane (22a): Compound **22a** was prepared by following the procedure described for the synthesis of **21a** to yield 1.01 g (90 %) as a white solid; M.p. 238–240 °C; ^1H NMR (500 MHz, $(CDCl_3)$): $\delta = 0.36$ (s, 12H; $SiCH_3$), 1.09 (s, 18H; CCH_3), 1.25 (br, 8H; CH_2), 1.53 (br, 4H; CH_2), 1.9–3.0 (br, 16H; BH), 2.26 (t, $^3J(H,H) = 8.5$ Hz, 4H; CCH_2), 3.72, 3.73 (s, 6H; CH_3), 6.68, 6.71 (d, $^3J(H,H) = 8.6$ Hz, 4H; C_6H_4), 7.13 ppm (d, $^3J(H,H) = 8.6$ Hz, 8H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = -2.1$ ($SiCH_3$), 20.6 (SiC), 27.8 (CCH_3), 29.2, 29.4, 30.5 (CH_2), 37.3 (CCH_2), 55.1, 55.12 (CH_3), 68.8($SiC_{carboranyl}$), 76.0 ($CC_{carboranyl}$), 113.0, 113.02, 133.9, 134.3, 158.9, 159.0 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -10.3$ (12B), -7.3 (4B), 6.6 (2B), 10.2 ppm (2B); MS (positive ion FAB): calcd for $C_{52}H_{90}B_{20}O_4Si_2$: 1051.6; found: m/z: 1053.1 [M^++H].

Synthesis of 1,8-Bis(9′,12′-di(4-methoxyphenyl)1′,2′-carboranyl)octane (22b): Compound **22b** was prepared following the procedure described for the synthesis of **20b** to yield 0.65 g (87 %) as a white solid. M.p. 196–198 °C; ^1H NMR (400 MHz, $(CDCl_3)$): $\delta = 1.28$ (br, 8H; CH_2), 1.5 (br, 4H; CH_2), 1.9–3.0 (br, 16H; BH), 2.28 (t, $^3J(H,H) = 8.6$ Hz, 4H; CCH_2), 3.60 (s, 2H; CH), 3.73, 3.74 (s, 6H; CH_3), 6.68, 6.70 (d, $^3J(H,H) = 8.6$ Hz, 4H; C_6H_4), 7.13, 7.15 ppm (d, $^3J(H,H) = 8.6$ Hz, 4H; C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 29.0$, 29.1, 29.5 (CH_2), 37.5 (CCH_2), 55.1, 55.12 (CH_3), 55.7 ($HC_{carboranyl}$), 69.7 ($CC_{carboranyl}$), 113.0, 134.2, 134.4, 159.06, 159.08 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -13.1$ (12B), -9.1 (4B), 5.1 (2B), 8.1 ppm (2B).

Synthesis of cyclic dimer 29c and cyclic tetramer 29a: *n*-Butyllithium (0.51 mL, 1.17 mmol, 2.3 M in hexane) was added dropwise to a solution of **22b** (0.459 g, 0.558 mmol) in THF (30 mL) at 0 °C. After stirring for 4 h at room temperature 1,8-dibromooctane (0.32 mL, 3.16 mmol) was added, and the solution was refluxed for 2 days. Then the reaction mixture was washed with brine, the aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under vacuum providing a white solid which was recrystallized in acetone to give 185 mg (71 %) of **29c** and 47 mg (9 %) of **29a**.

29c: ^1H (500 MHz, $CDCl_3$): $\delta = 1.34$ (m, 16H; CH_2), 1.58 (m, 8H; CH_2), 1.9–3.1 (br, 16H; BH), 2.25 (t, $^3J(H,H) = 8.6$ Hz, 8H; CCH_2), 3.73 (s, 12H; CH_3), 6.68 (d, $^3J(H,H) = 8.6$ Hz, 8H; C_6H_4), 7.14 ppm (d, $^3J(H,H) = 8.6$ Hz, 8H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 28.2$, 28.9, 29.4 (CH_2), 34.4 (CCH_2), 55.1 (CH_3), 73.9 ($C_{carboranyl}$), 113.0, 134.3, 159.0 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -10.0$ (16B), 5.9 ppm (4B); MS (positive ion FAB): calcd for $C_{48}H_{76}B_{20}O_4$: 933.35; found: m/z: 933.24 [M^+].

29a: ^1H (500 MHz, $CDCl_3$): $\delta = 1.31$ (br, 32H; CH_2), 1.56 (br, 16H; CH_2), 1.9–3.1 (br, 32H; BH), 2.20 (t, $^3J(H,H) = 8.6$ Hz, 16H; CCH_2), 3.72 (s, 24H; CH_3), 6.68 (d, $^3J(H,H) = 8.6$ Hz, 16H; C_6H_4), 7.13 ppm (d, $^3J(H,H) = 8.6$ Hz, 16H; C_6H_4); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 29.2$, 29.4, 30.0 (CH_2), 34.6 (CCH_2), 55.1 (CH_3), 73.8 ($C_{carboranyl}$), 113.1, 134.3, 159.1 ppm (C_6H_4); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -10.1$ (16B), 6.1 ppm (4B); MS (positive ion FAB): calcd for $C_{96}H_{152}B_{40}O_8$: 1866.70; found: m/z: 1867.85 [M^++H].

4,4′-Bis[(2′-(*tert*-butyldimethylsilyl)-9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)methyl]-4,4′-biphenylene (23a): Compound **23a** was prepared by following the procedure described for the synthesis of **21a**. Final purification was achieved by chromatography on silica gel with CH_2Cl_2/pentane (3:2) as the eluting solvent to yield **23a** as a white solid (58 mg, 80 %). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.51$ (s, 12H; $SiCH_3$), 1.21 (s, 18H; CCH_3), 1.9–3.0 (br, 16H; BH), 3.61 (s, 4H; CCH_2), 3.69, 3.73 (s, 6H; CH_3), 6.62, 6.67 (d, $^3J(H,H) = 8.6$ Hz, 4H; BC_6H_4), 7.03, 7.12 (d, $^3J(H,H) = 8.6$ Hz, 4H; BC_6H_4), 7.26, 7.53 ppm (d, $^3J(H,H) = 8.6$ Hz, 4H; $CH_2C_6H_4$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = -1.8$ ($SiCH_3$), 20.8 (SiC), 27.9 (CCH_3), 42.7 (CH_2), 55.04, 55.07 (CH_3), 67.9 ($SiC_{carboranyl}$), 75.8 ($CC_{carboranyl}$), 112.9, 112.96, 133.9, 134.3, 158.92, 158.95 (BC_6H_4), 127.5, 130.5, 135.3, 140.2 ppm ($CH_2C_6H_4$); ^{11}B NMR (160 MHz, $CDCl_3$): $\delta = -10.4$ (12B), -7.5 (4B), 6.8 (2B), 10.3 ppm (2B); MS (positive ion FAB): calcd for $C_{58}H_{86}B_{20}O_4Si_2$: 1119.8; found: m/z: 1119.6 [M^+].

4,4′-Bis[(9′,12′-di(4-methoxyphenyl)-1′,2′-carboranyl)methyl]-4,4′-biphenylene (23b): Compound **23b** was prepared by following the procedure described for the synthesis of **20b** to yield 1.52 g (91 %) as a white solid. M.p. 293–295 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.9–3.0$ (br, 16H; BH), 3.35 (s, 2H; CH), 3.67 (s, 4H; CCH_2), 3.71, 3.73 (s, 6H; CH_3), 6.66, 6.69 (d, $^3J(H,H) = 8.7$ Hz, 4H; BC_6H_4), 7.10, 7.13 (d, $^3J(H,H) = 8.7$ Hz, 4H; BC_6H_4), 7.28, 7.61 ppm (d, $^3J(H,H) = 8.7$ Hz, 4H; $CH_2C_6H_4$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 42.7$ (CH_2), 55.11, 55.13 (CH_3), 54.2 ($HC_{carboranyl}$), 77.4 ($CC_{carboranyl}$), 113.06, 113.08, 134.2, 134.4, 159.1, 159.13 (BC_6H_4), 127.8, 130.6, 135.9, 140.4 ppm ($CH_2C_6H_4$); $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -10.4$ (12B), -7.5 (4B), 6.8 (2B), 10.3 ppm (2B); HRMS (EI): calcd for $^{12}C_{46}{}^1H_{58}{}^{11}B_{20}{}^{16}O_4$: 891.6340; found: m/z: 891.6328 [M^+] ($\Delta = 1.2$ mmu).

α,α′-Bis(2′-(*tert*-butyldimethylsilyl)-9′,12′-di(4-methoxyphenyl)-1′,2′-carboraniyl)lutidine (24a): Compound **24a** was prepared by following the procedure described for the synthesis of **21a** with the exception that the time at reflux was extended to 2 days. Purification by chromatography on silica gel with toluene/CH_2Cl_2 (3:1) as the eluting solvent led to **24a** as a

white solid (0.90 g, 81%). M.p. 246–247 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 0.58$ (s, 12H; $SiCH_3$), 1.25 (s, 18H; CCH_3), 1.9–3.1 (br, 16H; BH), 3.64, 3.67 (s, 6H; CH_3), 3.91 (s, 4H; CH_2), 6.57, 6.64 (d, $^3J(H,H) = 8.7$ Hz, 4H; C_6H_4), 6.99, 7.10 (d, $4^3J(H,H) = 8.6$ Hz, H; C_6H_4), 7.31 (d, 2H; $^3J(H,H) = 7.7$ Hz, C_5H_3N), 7.71 ppm (t, $^3J(H,H) = 7.7$ Hz, 1H; C_5H_3N); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$): $\delta = -1.83$ ($SiCH_3$), 21.2 (SiC), 28.2 (CCH_3), 45.0 (CH_2), 55.0 (CH_3), 68.9 ($SiC_{carboranyl}$), 75.7 ($CC_{carboranyl}$), 113.51, 113.53, 134.5, 134.8, 159.8, 159.9 (C_6H_4), 124.8, 138.7, 156.9 ppm (C_5H_3N); $^{11}B\{^1H\}$ NMR (160 MHz, THF): $\delta = -10.6$ (12B), −7.8 (4B), 6.6 (2B), 9.9 ppm (2B); MS (positive ion FAB): calcd for $C_{51}H_{81}B_{20}NO_4Si_2$: 1044.89; found: m/z: 1044.6 $[M^+]$.

α,α′-Bis(9′,12′-di(4-methoxyphenyl)-1′,2′-carboraniyl)lutidine (24b): Compound **24b** was prepared by following the procedure described for the synthesis of **20b**. Purification by chromatography on silica gel with CH_2Cl_2 as the eluting solvent led to **24b** as a white solid (683 mg, 99%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 1.9–3.0$ (br, 18H; BH), 3.66, 3.67 (s, 6H; CH_3), 3.94 (s, 4H; CH_2), 4.79 (s, 2H; CH), 6.63, 6.64 (d, $^3J(H,H) = 8.7$ Hz, 4H; C_6H_4), 7.06, 7.07 (d, $^3J(H,H) = 8.4$ Hz, 4H; C_6H_4), 7.44 (d, $^3J(H,H) = 7.7$ Hz, 2H; C_5H_3N), 7.88 ppm (t, $^3J(H,H) = 7.7$ Hz, 1H; C_5H_3N); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$): $\delta = 44.7$ (CH_2), 55.1 (CH_3), 56.1 ($HC_{carboranyl}$), 69.5 ($CC_{carboranyl}$), 113.55, 113.57, 134.7, 134.9, 159.98, 160.0 (C_6H_4), 124.9, 139.3, 156.7 ppm (C_5H_3N); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = -11.4$ (12B), −8.9 (4B), 6.6 (2B), 9.4 ppm (2B); HRMS (EI): calcd for $^{12}C_{39}{}^1H_{53}{}^{11}B_{20}{}^{14}N_1{}^{16}O_4$: 815.6004; found: m/z: 815.5965 $[M^+]$ ($\Delta = 3.9$ mmu).

Synthesis of cyclic tetramer 30a: *n*-Butyllithium (0.237 mL, 0.592 mmol, 2.5 M in hexane) was added dropwise to a solution of **24b** (230 mg, 0.28 mmol) in THF (30 mL) at 0 °C. After stirring for 4 h at room temperature, α,α′-dibromo-2,6-lutidine (73 mg, 0.28 mmol) was added, and the solution was refluxed for 2 days. Then the reaction mixture was washed with brine, the aqueous layer was extracted with diethyl ether (3×50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under vacuum providing a white solid, which was recrystallized in CH_2Cl_2/THF to give 52 mg (10%) of **30a**; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 3.65$ (s, 24H; CH_3), 6.66, 7.04 (d, $^3J(H,H) = 8.1$ Hz, 32H; C_6H_4), 7.25, 7.77 ppm (br, 12H; C_5H_3N); $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$): $\delta = 43.1$ (CH_2), 55.2 (CH_3), 113.7, 134.8, 160.1 (C_6H_4), 125.0, 139.0, 157.0 ppm (C_5H_3N); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = -9.2$ (32B), 7.0 ppm (8B); MS (positive ion FAB): calcd for $C_{92}H_{116}B_{40}N_4O_8$: 1838.28; found: m/z: 1838.28 $[M^+]$.

X-ray crystallography. A summary of the crystallographic data and details of the structure determinations is given in Tables 1 and 2. Data were collected on a Bruker Smart CCD diffractometer (**27a**, **28b**, **30a**) ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\theta + 2\theta$ scans), a Syntex-$P\bar{1}$ diffractometer (**1**, **12**, **28a**) ($Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\theta - 2\theta$ scans), and a Huber Crystal Logic (**3**, **6**) diffractometer ($Mo_{K\alpha}$ radiation, $\theta - 2\theta$ scans). Data were corrected for Lorentz and polarization effects, and for secondary extinction. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 (SHELX93 and 86). In all structures atoms were located by use of direct methods. Scattering factors for H were obtained from Stewart et al.[38] and for other atoms were taken from ref. [39] CCDC-202913 (**1**), CCDC-202914 (**3**), CCDC-202915 (**6**), CCDC-202916 (**12**), CCDC-202917 (**27a**), CCDC-202918 (**28a**), CCDC-202919 (**28b**), CCDC-202920 (**30a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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