Synthesis, Structure, and Reactivity of *closo*-2,3,4,5,6,7,8,9,10,11-Decahydroxy-1,12-bis(sulfonic acid)-1,12-dicarbadodecaborane(12)

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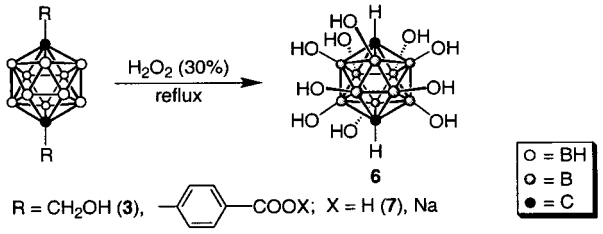
Abstract: The reaction of *closo*-1,12-bis(lithio)-1,12-dicarbadodecaborane(12) (1,12-bis(lithio)-*p*-carborane) with SO_2 formed *closo*-1,12-bis(lithiosulfinato)-*p*-carborane (**10**) in nearly quantitative yield. The latter was converted to *closo*-1,12-bis(sulfinic acid)-*p*-carborane (**13**) via H^+-exchange. The corresponding 1,12-bis-(sulfonic acid) derivative of *p*-carborane (**12**) was obtained in high yield by treating **10** with SO_2Cl_2 and subsequent $AlCl_3$ mediated hydrolysis of the *closo*-1,12-bis(chlorosulfonyl)-*p*-carborane intermediate. The exhaustive oxidation of **12** in hot aqueous H_2O_2 (30%) afforded *B*-decahydroxy-1,12-bis(sulfonic acid)-*p*-carborane (**15**) in 40% yield. As a byproduct, *closo*-*B*-decahydroxy-1-sulfonic acid-*p*-carborane (**14**) was formed. Both **14** and **15** were also obtained from the hydroxylation of **10** and **13**. Compound **14** was obtained directly in 88% yield by heating 1-sulfinic acid-*p*-carborane (**17**) in H_2O_2 (30%). Compound **17** was synthesized from diphenylmethylsilyl-protected *p*-carborane by using the method employed in the synthesis of **13**. The X-ray structures of **15**, its disodium salt, and its dipotassium salt are presented and discussed. Exhaustive methylation of **15** with methyl triflate furnishes *closo*-*B*-decamethoxy-1,12-bis(methyl sulfonate)-*p*-carborane (**20**). The characterization of closomer **20** also includes its crystal structure determination.

Introduction

Recent research led to the discovery that the icosahedral boranes Cs_2[*closo*-$B_{12}H_{12}$] (**1**), Cs[*closo*-$CB_{11}H_{12}$] (**2**), and *closo*-1,12-$(HOCH_2)_2$-1,12-$C_2B_{10}H_{10}$ (**3**) form the *B*-perhydroxylated species Cs_2[*closo*-$B_{12}(OH)_{12}$] (Cs_2**4**), Cs[*closo*-1-H-1-CB_{11}-$(OH)_{11}$] (Cs**5**), and *closo*-1,12-$(H)_2$-1,12-$C_2B_{10}(OH)_{10}$ (**6**) (Scheme 1) when heated in aqueous 30% H_2O_2.[1,2] These icosahedral species containing aromatic 26-electron cages represent a novel class of so-called camouflaged polyhedral borane derivatives.[3] Consequently, the question was raised whether the spherical sheath of hydroxyl groups in **4**−**6** can serve as cores for the synthesis of dendrimer-like derivatives[1,3,4] (extended *closomers*[5,6]). In the case of **4** the first step in this direction has been successfully taken. Very recently it has been demonstrated that **4** can be fully acetylated by using acetic acid anhydride or completely benzoylated when benzoyl chloride was reacted with $[(n\text{-Bu})_4N]_2$**4**.[5] Furthermore, the dodecabenzyl ether derivative of **4** was obtained by reacting $[PPN]_2$**4** and benzyl chloride in the presence of Hünigs base.[6] Subsequently, the *closomer* $[B_{12}(OCH_2Ph)_{12}]^{2-}$ could be reversibly oxidized in two, one-electron steps to the corresponding neutral *hyperclosomer*.[6]

The reactivity of Cs**5** has not yet been investigated, mainly due to its availability in only relatively low yield combined with the scarcity of the carborane precursor. Meanwhile, the utility of **6** as a reagent is limited by its extremely poor solubility in all common organic solvents as well as water. However, for the following reasons we were motivated to further investigate the chemistry of **6**. Among the three *B*-perhydroxy derivatives **4**−**6**, compound **6** can be obtained in the highest yield (80%). More importantly, **6** contains two CH vertices which enhance its availibility in organic syntheses. Hydrophilic substituents at the 1- and 12-positions of **6** should improve the solubility of the resulting *B*-decahydroxylated carborane and provide two distinguishable reactive sites in a hypothetical extended closomer structure.

Scheme 1



Reported here are reactivity studies of **6** and the syntheses of sulfinates and sulfonates of *p*-carborane as suitable precursor compounds for conversion to the water-soluble 1-mono- and 1,12-bis(sulfonic acid) derivatives of *closo*-*B*-decahydroxy-*p*-carborane. Structural features of *closo*-*B*-decahydroxy-*p*-carborane-1,12-bis(sulfonic acid) are compared to those found for **6**.

Results and Discussion

Reactivity of 6. Initially, it was found that **6** remains insoluble and unchanged when heated in aqueous concentrated NaOH solution or 6 M H_2SO_4. In formally viewing **6** as a polysac-

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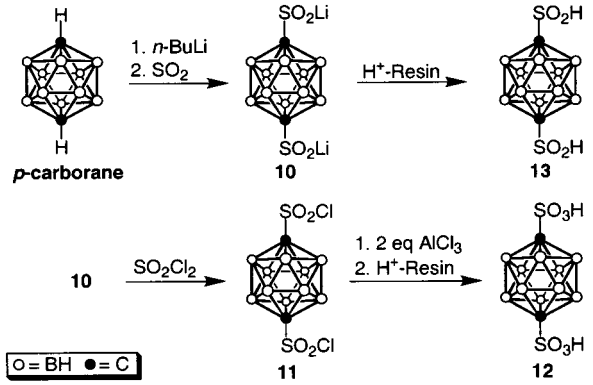
charide, characteristic functionalizations were attempted. However, methylation under neither phase transfer conditions with dimethyl sulfate[7] nor with lithium methyl sulfinyl methylide and methyl iodide[8] were successful. A suspension of **6** in liquid ammonia in the presence of 2 equiv of dissolved sodium metal did not react. Efforts to esterify **6** by treating it with neat benzoic- or triflic anhydride at elevated temperatures failed as did reactions of **6** with various carboxylic acid chlorides, with or without an added base. A suspension of **6** in neat chloro sulfonic acid yielded a clear yellow solution at its boiling temperature but the resulting mixture of *closo*-carborane, as well as boric acid derivatives, likely sulfates, was inseparable. Given the chemical inertness of **6**, we focused on the introduction of substituents at the 1- and 12-vertices of *p*-carborane which would be retained during the BH-hydroxylation reaction.

Previously, the exhaustive hydroxylation of *p*-carborane by H_2O_2 was achieved by using the poorly water-soluble diol **3** as a precursor (Scheme 1). The loss of the $-CH_2OH$ functions during the oxidation suggests their conversion to $-COOH$ groups and subsequent decarboxylation. As an alternative, carboxylic acid functions were placed well away from the cage carbon vertices using a substituent that is more robust toward oxidation. *closo*-1,12-Bis(4-carboxyphenyl)-*p*-carborane[9] (**7**) as well as its disodium salt were reacted in excess H_2O_2 (30%) at 90 °C. These reactions proceeded vigorously and were completed within 3 h (^{11}B NMR)—about 4 times faster than found for the *B*-perhydroxylation of **3**. Again the complete loss of the C-substituents occurred and **6** was formed in 35% yield (Scheme 1).

Reasoning that carbon-containing groups cannot withstand the harsh oxidation conditions required for hydroxylation, inorganic derivatives of *p*-carborane such as C-sulfonic acids were pursued as suitable precursors for the BH-hydroxylation reaction.

Synthesis of Sulfinic and Sulfonic Acid Derivatives of *p*-Carborane and Their BH-Hydroxylation. Generally, sulfonic acids are known to exhibit excellent solubility properties in aqueous media. The sulfur atom already possesses its highest formal oxidation state and the sulfur−carbon bond is known to be very stable.[10] Although previous studies of the oxidation of the SH-groups of 1,7- and 1,12-bis(thiol)-substituted *m*- and *p*-carborane have been reported,[11−13] 1,12-sulfinic and sulfonic acid derivatives of *p*-carborane had not yet been prepared. The synthesis of *closo*-1,7-$(HO_3S)_2$-1,7-$C_2B_{10}H_{10}$ (**8**),[11] also the subject of a patent,[14] has been accomplished by a stepwise oxidative conversion of the parent 1,7-bis(thiol) to the corresponding *closo*-1,7-bis(chlorosulfenyl)- and *closo*-1,7-bis(chlorosulfonyl)-*m*-carborane, respectively. With the assistance of $AlCl_3$, the latter compound was hydrolyzed to **8**. Monosulfinic acid derivatives of *o*-carborane including *closo*-1-HO_2S-1,2-$C_2B_{10}H_{11}$ (**9**) have been prepared by reacting the lithiated carborane with SO_2.[15] It was reported that **9** eliminates SO_2 when heated in H_2O.[15]

Scheme 2



The synthesis of the *p*-carborane analogue of **8** started by preparing *closo*-1,12-bis(lithio sulfinato)-*p*-carborane (**10**) by reacting bis(lithio)-*p*-carborane with SO_2. The reaction of **10** with SO_2Cl_2[16] furnished *closo*-1,12-bis(chlorosulfonyl)-*p*-carborane (**11**) in quantitative yield. Use of the $AlCl_3$-mediated hydrolysis of **11**, analogous to the procedure employed in the synthesis of **8**,[12] afforded the bis(sulfonic acid) *closo*-1,12-$(HO_3S)_2$-1,12-$C_2B_{10}H_{10}$ (**12**) in 95% yield. In parallel, the corresponding bis(sulfinic acid) *closo*-1,12-$(HO_2S)_2$-1,12-$C_2B_{10}H_{10}$ (**13**) was obtained as an air-stable compound after H^+-cation exchange of **10** (Scheme 2).

As expected, the three species, **12**, **13**, and **10**, are quite water-soluble. Their reactions with 30% H_2O_2 were studied in the given order with the assumption that the sulfinates would be converted to the sulfonic acids under the hydroxylation reaction conditions.[17] Hydroxylation of **12** with excess 30% H_2O_2 at the reflux temperature was completed within 5.5 h. Three products, boric acid (20%, singlet in the ^{11}B NMR spectrum at 20 ppm), an unidentified borate (20%, singlet in the ^{11}B NMR spectrum at −4 ppm), and the *B*-perhydroxylated carborane derivative (60%, broad singlet in the ^{11}B NMR spectrum at −16 ppm), formed. In contrast to the hydroxylation of **3** (**6** precipitated and could be isolated by filtration) the products from the hydroxylation of **12** remained in solution. Their isolation required the decomposition of all residual peroxide prior to the drying step. It was found that a peroxide-free solution was obtained by treatment of the reaction mixture with an excess of concentrated HBr at 80 °C for 12 h. Furthermore, ^{11}B NMR spectra indicated that this procedure had no influence upon the identity (chemical shift) nor the distribution (integration ratios) of the products. Upon removal of all volatiles in vacuo the products were partitioned in accord with their solubilities in methanol. The methanol-insoluble residue was identified as *closo-B*-decahydroxy-1-sulfonic acid-*p*-carborane (**14**, 15%) whereas, to our surprise, the desired *closo-B*-decahydroxy-1,12-bis(sulfonic acid)-*p*-carborane (**15**) crystallized from the methanol extract (45% yield)[18] (Scheme 3). The boric acid byproducts and minor amounts of incompletely hydroxylated carborane remained dissolved in the methanol. Both **14** and **15**

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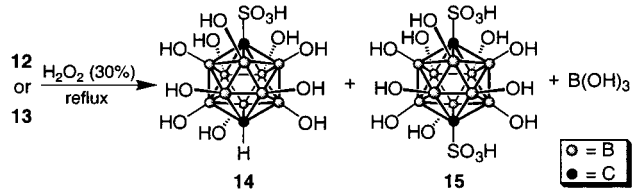
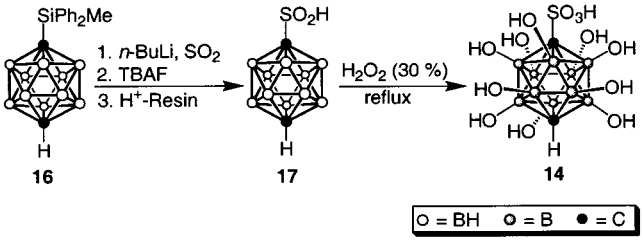
(18) Upon standing in methanol another solid phase of **15** precipitates over time. A swift workup to separate **14** from **15**, as described herein, is recommended.

Scheme 3



Scheme 4



are quite soluble in H_2O and were found to be stable in aqueous base (NaOH).

The hydroxylation of **13** as well as the workup procedure was conducted according to the protocol described for the oxidation of **12**. While the reaction time for complete hydroxylation of **13** was found to be essentially the same as that observed for **12**, more **14** (25%) was formed relative to **15** (35%).

The oxidation of **10** was completed within 2 h, but the yield of hydroxylated derivative was only 30%. This result suggests a dependence of the rates of hydroxylation and product degradation upon pH.

The superb water solubility of **14** encouraged the development of a synthetic method that allows its preparation in higher yield. Reaction of monolithiated *closo*-1-Ph_2MeSi-1,12-$C_2B_{10}H_{11}$ (**16**) with SO_2, subsequent desilylation with [(*n*-Bu)$_4$N]F in THF at 50 °C, followed by flash chromatography with Et_2O/methanol yielded the (*n*-Bu)$_4$N-salt of *closo*-1-sulfinic acid-*p*-carborane. Cation exchange (H^+) furnished the *p*-carborane analogue of **9**, **17**, as a colorless solid (Scheme 4). The sulfinic acid **17** slowly turns brown upon prolonged exposure to air. A two-week old sample displayed a broadening of the resonance comprising its ^{11}B NMR spectrum and a mass spectrum (FAB, negative mode) contained the parent peak of the *closo*-1-sulfonate-*p*-carborane anion. However, the corresponding ^{13}C NMR spectrum did not show significant changes. Nevertheless, it can be assumed that **17** decomposes slowly according to $3RSO_2H \rightarrow RSO_2SR + RSO_3H + H_2O$.[19]

Hydroxylation of a freshly prepared sample of **17** in H_2O_2 (30%) at the reflux temperature was completed after 3.5 h and the ^{11}B NMR spectrum of the crude reaction mixture indicated the formation of **14** in approximately 90% yield, later confirmed by mass balance after workup (HBr). Aside from $B(OH)_3$ (3%) and unidentified borate (3%) only small amounts of **6** were isolated (5%). Astonishingly, the loss of SO_2, observed during the hydroxylation of **12** and **13** and more significantly in the case of **9** in hot H_2O,[15] is negligible in this instance.

Structural Characterization of 15 and Its Disodium and Dipotassium Salts. The striking dissimilarity of the solubility properties of **6** versus **15** prompted us to investigate the solid-state structure of the latter compound. Additionally, X-ray diffraction analyses were performed on the disodium salt and the dipotassium salt of **15** (**18** and **19**, respectively), which explains the significant decrease in their water solubility compared to **15**.

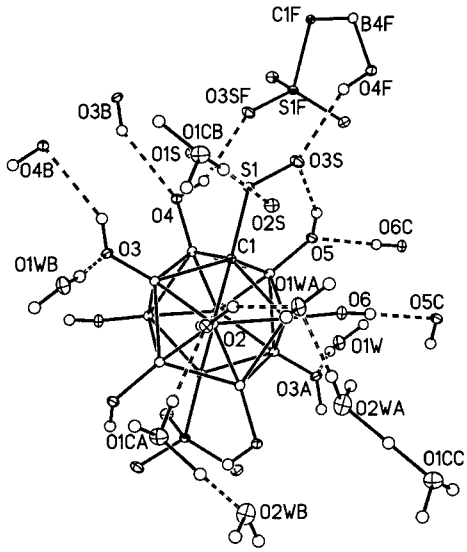


Figure 1. ORTEP diagram of a portion of the structure of **15**. The ellipsoids represent a 30% probability level. Fragments of the neighboring icosahedra (B, C, and F) are shown to demonstrate intermolecular O−H···O interactions. Selected bond lengths [pm]: B−O 138.3(2)−139.7(2); B−B 177.1(2)−185.0(2); B−C 172.9(2)−177.5(2); C(1)−S(1) 181.9(5).

Structural Characterization of 15. Crystals of **15** obtained from methanol were suitable for an X-ray diffraction study (Table 1). The structure, depicted in Figure 1, shows that the counterions of the sulfonate functions of **15** are hydronium ions. Diacid **15** crystallizes as a tetrahydrate in the triclinic space group *P-1*, and is centrosymmetric. All ten hydroxyl hydrogen atoms are involved in hydrogen bonds to water, other hydroxyl group oxygen atoms (intermolecular), or two oxygen atoms of the SO_3^--moieties (intramolecular). One type of water molecule is bonded via its two hydrogen atoms to oxygen atoms of a hydroxyl group and an SO_3^--oxygen, and it also forms hydrogen bridges to another water molecule as well as to a hydroxyl group. The other type of water molecule is bonded via its two hydrogen atoms to oxygen atoms of a hydroxyl group and a water molecule, and it is also hydrogen bonded to the hydronium cation. Additionally, the cation displays hydrogen bridges to an SO_3^--oxygen and a hydroxyl group.

Structural Characterization of the Disodium Salt of 15, 18. Single crystals of **18** were obtained from a dilute solution of **15** in 2 M aqueous NaOH. Figure 2 shows the structure of one of the four centrosymmetric dianions contained per unit cell. The salt crystallizes in the monoclinic space group *C*2/*c* with four molecules of water per dianion (Table 1). As found in Na_2**4**,[2] each sodium cation is octahedrally ligated by six oxygen atoms. On a 2-fold axis, Na1A is coordinated by oxygen atoms of two water molecules, two SO_3^--groups, and two hydroxyl groups. Na2X, on a center of symmetry, interacts with oxygen atoms of four hydroxyl groups and two SO_3^--moieties. All ten hydroxyl hydrogen atoms are involved in hydrogen bonds to water (two), other hydroxyl group oxygen atoms (two), or oxygen atoms of the SO_3^--moieties (six). One water molecule is bonded via its two hydrogen atoms to oxygen atoms of a hydroxyl group and a water oxygen, and it also forms a hydrogen bridge to a hydroxyl group. The other water molecule is bonded via one of its two hydrogen atoms to an oxygen atom of a SO_3^--group.

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Table 1. Crystal Data, Data Collection, and Refinement Parameters[a]

	15·$(H_2O)_6$	**18**·$(H_2O)_4$	**19**·$(H_2O)_4$	**20**
empirical formula	$C_2H_{24}B_{10}O_{22}S_2$	$C_2H_{18}B_{10}Na_2O_{20}S_2$	$C_2H_{14}B_{10}K_2O_{18}S_2$	$C_{14}H_{36}B_{10}O_{16}S_2$
formula wt	572.43	580.36	576.55	632.65
T, K	100(2)	100(2)	298(2)	298(2)
crystal size, mm^3	0.35 × 0.45 × 0.5	0.02 × 0.1 × 0.6	0.05 × 0.1 × 0.3	0.45 × 045 × 0.1
color, habit	colorless parallelepiped	colorless needle	colorless parallelepiped	colorless plate
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	*P-1*	*C*2/*c*	*C*2/*m*	$P2_1/c$
cell dimensions:				
a, Å	7.4735(14)	16.282(5)	12.3129(18)	15.5395(15)
b, Å	7.9376(15)	7.343(2)	10.0702(13)	13.5678(14)
c, Å	9.5097(18)	16.735(5)	8.8975(12)	13.6715(14)
α, deg	77.594(4)	90	90	90
β, deg	73.677(3)	102.579(5)	126.471(2)	93.092(2)
γ, deg	68.076(3)	90	90	90
V, $Å^3$	498.40(16)	1952.9(10)	887.2(2)	2878.3(5)
Z	1	4	2	4
ρ_{calcd}, g/cm^3	1.907	1.974	2.158	1.460
abs coeff, mm^{-1}	0.378	0.419	0.867	0.255
F(000)	294	1176	580	1320
θ range, deg	2.25 to 28.28	2.49 to 28.29	2.85 to 28.29	1.31 to 28.31
index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-12 \le l \le 8$	$-21 \le h \le 20$, $-7 \le k \le 9$, $-21 \le l \le 22$	$-16 \le h \le 14$, $-13 \le k \le 10$, $-10 \le l \le 11$	$-14 \le h \le 20$, $-18 \le k \le 12$, $-17 \le l \le 17$
no. of reflcns collected	3290	6209	2957	18871
no. of independent reflcns	2276 ($R_{int} = 0.0355$)	2335 ($R_{int} = 0.0340$)	1121 ($R_{int} = 0.0216$)	6967 ($R_{int} = 0.0243$)
completeness to θ_{max}	91.4%	96.5%	95.9%	97.4%
abs corr	none	none	SADABS	SADABS
no. of data/restraints/ parameters	2276/0/199	2335/3/193	1121/0/99	6967/0/438
goodness-of-fit on F^2	1.058	0.962	0.516	0.994
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0296$, $wR_2 = 0.0810$	$R_1 = 0.0342$, $wR_2 = 0.0779$	$R_1 = 0.0263$, $wR_2 = 0.0705$	$R_1 = 0.0794$, $wR_2 = 0.2118$
R indices (all data)	$R_1 = 0.0301$, $wR_2 = 0.0814$	$R_1 = 0.0594$, $wR_2 = 0.0852$	$R_1 = 0.0298$, $wR_2 = 0.0745$	$R_1 = 0.1005$, $wR_2 = 0.2386$
extinction coeff	none	0.0000(3)	0.0028(10)	none
larg. diff peak, hole, $eÅ^{-3}$	0.459 and −0.535	0.555 and −0.431	0.424 and −0.530	1.64 and −0.28

[a] Details in common: Mo Kα radiation ($\lambda = 0.71073$ Å), *φ* and *ω* scans, Bruker SMART CCD diffractometer. Refinement method: full-matrix least-squares on F^2. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

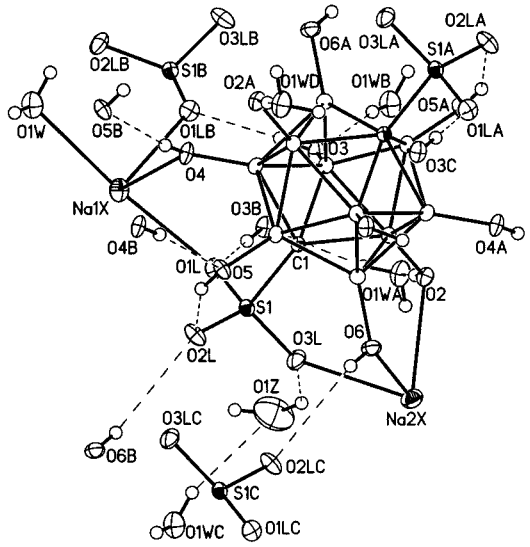


Figure 2. ORTEP diagram of a portion of the structure of **18**. Half of the symmetrical coordination sphere of each sodium cation (Na1X and Na2X) is shown. Additional fragments of adjacent cages are included to display relevant coordination sites and hydrogen bridges. The ellipsoids represent a 30% probability level. Selected bond lengths [pm]: B−O 137.7(3)−139.1(3); B−B 175.6(4)−183.6(4); B−C 174.0(3)−178.7(4); C(1)−S(1) 182.4(2).

Structural Characterization of the Dipotassium Salt of 15, 19. Figure 3 shows the structure of one centrosymmetric dianion of **19**. The compound crystallizes in the monoclinic space group *C*2/*m* with four molecules of water per dianion (Table 1). Contrary to sparingly soluble K_2**4** (coordination of the potassium cations by seven hydroxyl oxygen atoms),[2] the potassium cations in **19** are surrounded by ten oxygen atoms, four from SO_3^--groups and six from hydroxyl groups. Only the remaining four of the ten hydroxyl hydrogen atoms are involved in hydrogen bonds to water or oxygen atoms of the SO_3^--moieties. One water molecule bridges two hydroxyl groups via hydrogen bonding of its hydrogen atoms to their oxygen atoms.

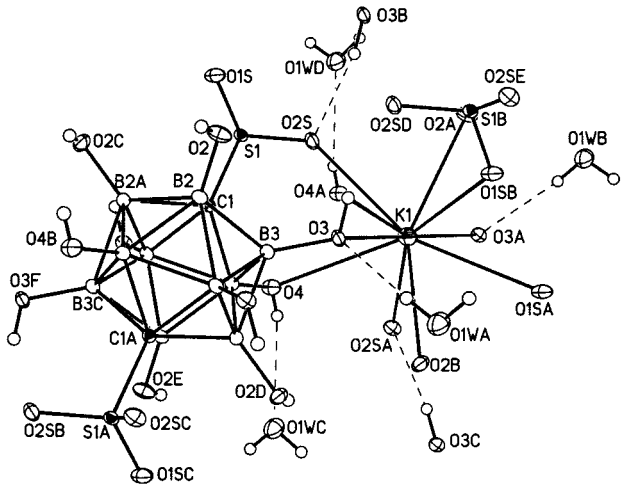


Figure 3. ORTEP diagram of a portion of the structure of **19**. Only one of the two symmetrically coordinated potassium cations is shown. Additional fragments from nearby cages are depicted to exhibit the entire coordination sphere of the cation. The ellipsoids represent a 30% probability level. Selected bond lengths [pm]: B−O 138.9(2)−139.2(2); B−B 176.1(2)−184.1(2); B−C 172.3(3)−176.8(2); C(1)−S(1) 182.9(2).

The structure of **15** illustrates its high affinity for the water molecules and hydronium ions surrounding the icosahedron, thus reflecting its propensity for solvation by water molecules in solution. In **18** and **19**, the hydroxylated icosahedra are linked to a polymeric network via the alkali cations. Apparently, the lattice energy of **19** exceeds by far the hydration enthalpy of the 10-fold oxygen-coordinated potassium cation. Here, the lack of participation of hydroxyl groups in this network results in its low solubility in water as does the participation of all hydroxyl groups in the network of **6**.

The B−O bond lengths in **15** (138.3(2)−139.7(2) pm), **18** (137.7(3)−139.1(3) pm), and **19** (138.9(2)−139.2(2) pm) are in the same range as those found in the solid-state structure of **6** (138.6(4)−140.3(4) pm). Furthermore, both the average tropical (vertical) and meridional (horizontal) B−B bond distances in **15**, **18**, and **19** are in the same range as in **6**. It is noteworthy that the meridional B−B bonds in all *closo-B*-decahydroxy-*p*-carborane species are about 3.8% longer compared to those of *p*-carborane (176.2(5) pm).[20] The same tendency and magnitude is observed in a comparison of the corresponding C−B bonds. However, the tropical B−B bonds in **6**, **15**, **18**, and **19** are only 1.5 pm or less than 1% longer than the comparable B−B bonds in *p*-carborane. This "ovalization" of the symmetrically substituted *p*-carborane cage has recently been described for *closo*-1,12-bis(ethynyl)-*p*-carborane[21] and can also be found in *closo*-1,12-$(F_3CS(O)_2OCH_2)_2$-1,12-$C_2B_{10}(CH_3)_{10}$.[22] In both of these cases ovalization was less developed. A further distortion of the *closo*-cages of **15**, **18**, and **19** originates from a slippage of the apical C-vertices relative to the meridional five-membered boron rings, causing the C−B bonds to differ in length by about 4.5 pm. Since the longer C−B bonds are found opposite the charged oxygen of the sulfonate group, the distortion may be the result of a *trans*-effect of electronic and steric oxygen. Conspicuously, the average C−S bond length for the carboranyl sulfonic acid derivatives (182.4(5) pm) exceeds those found for alkyl derivatives such as 2-(*N*-morpholino)ethane sulfonic acid (178.9(7) pm)[23] or sodium (4-aminophenyl)methane sulfonate (179.5(3) pm).[24] This finding may explain the tendency of the carborane sulfonates to facilely release SO_2. In summary, the structural analyses of **15**, **18**, and **19** suggest only an insignificant electronic influence of the SO_3^--functions on the carborane scaffold and consequently on the nucleophilicity of the *B*-hydroxyl oxygen atoms.

Reactivity Studies. It is imperative to note that two detonations occurred when treating *dry* samples of **14**, either upon scratching with a glass rod or heating while evacuating the containing vessel. Furthermore, **14** decomposes explosively when heated to temperatures near 325 °C. Thus, **14** must be categorized as a heat- and shock-sensitive substance. These hazardous properties may be explained by a SO_2 elimination accompanied by a subsequent oxidation of the cage by SO_2 in its *statu nascendi*.

Similary, **15** exhibits an explosive decomposition point of 230 °C. Hence, as in the case of **14**, **15** must be handled as a heat- and potentially shock-sensitive[25] compound. Furthermore, it was found that **15** explodes violently when in contact with neat acetic anhydride.

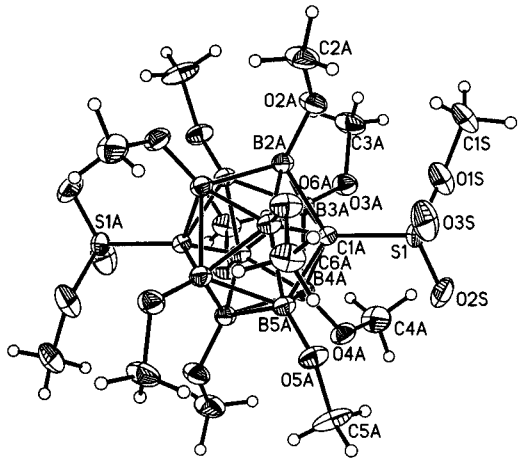
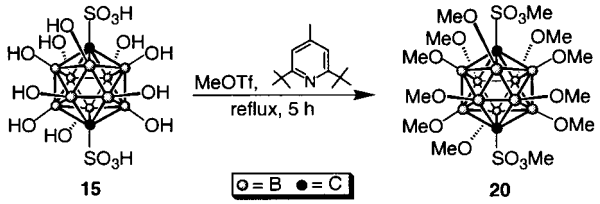


Figure 4. ORTEP diagram of the structure of **20**. Shown is one of the two noncrystallographically related molecules contained in the asymmetric unit, both of which are centrosymmetric. The molecule shown is not disordered whereas the second molecule of **20** is disordered with the $-SO_2OCH_3$ moieties in two different orientations, at 82% and 18% occupancy. The ellipsoids represent a 30% probability level. Selected bond lengths [pm]: B−O 136.9(3)−138.4(3); B−B 177.0(4)−185.2(4); B−C 174.5(3)−177.6(3); C(1A)−S(1) 178.5(5).

Scheme 5



Attempts to benzylate **15** in anhydrous DMSO with solid KOH and benzyl bromide[26] resulted in its complete decomposition to $B(OH)_3$. Similary, methylation of **15** under phase-transfer conditions with dimethyl sulfate and $[(n\text{-}Bu)_4N]OH$ in a benzene/water mixture[7] did not occur and **15** was recovered quantitatively. However, the reaction of the hexahydrate of **15** with neat methyl triflate in the presence of 2,6-di-*tert*-butyl-4-methylpyridine[27] led to the formation of *closo-B*-decamethoxy-1,12-bis(methyl sulfonate)-*p*-carborane (**20**; 82% yield after purification) (Scheme 5). Loss of sulfonate groups or other degradation reactions were not observed. Compound **20** is sparingly soluble in hexane, but soluble in polar organic solvents. The solid did not display explosive properties.

Structural Characterization of 20. Crystals of **20** obtained from acetone were suitable for an X-ray diffraction study (Table 1). The structure (Figure 4) confirmed that all hydroxyl groups of **15** are methylated. The B−C (174.5(3)−177.6(3) pm) and B−B bond lengths (177.0(4)−185.2(4) pm) in **20** do not differ significantly from the comparable distances in **6**, **15**, **18**, and **19**; hence, the same cage distortions are observed. The B−O bonds (136.9(3)−138.4(3) pm) in **20** are understandably about 1 pm shorter in **6**, **15**, **18**, and **19**. The C−S bond length in **20** (178.5(5) pm) is comparable with the C−S bond distance of

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(21) Batsanov, A. S.; Fox, M. A.; Howard, J. A. K.; MacBride, H. J. A.; Wade, K. *J. Organomet. Chem.* **2000**, *610*, 20−24.

(22) Herzog, A.; Knobler, C. B.; Hawthorne, M. F.; Maderna, A.; Siebert, W. *J. Org. Chem.* **1999**, *64*, 1045−1048.

(23) Christensen, A. N.; Hazell, R. G.; Lehmann, M. S.; Nielsen, M. *Acta Chem. Scand.* **1993**, *47*, 753−756.

(24) Lechat, J. R. *Acta Crystallogr. Sec. B* **1979**, *35*, 183−185.

(25) (a) Compound **15** did not detonate upon scratching. However, this does not preclude the occurrence of such an event when dealing with this species. (b) See preface of Experimental Section.

(26) (a) Benedict, D. R.; Bianchi, T. A.; Cate, L. A. *Synthesis* **1979**, 428−429. (b) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169−2173.

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the triflate ester *closo*-1,12-$(F_3CS(O)_2OCH_2)_2$-1,12-$C_2B_{10}(CH_3)_{10}$ (179.6(7) pm).[22] The C−O distances in **20** (141.1(3)−143.3(3) pm) are in the typical range of organic methoxy derivatives.

Conclusion

The exploratory study of *closo*-*B*-perhydroxyl-*p*-carborane presented here demonstrates that its C−H vertices can be utilized as platforms for substituents which control its solubility and reactivity. By placing sulfonate groups at the 1 and 12 positions of **6**, the methanol-soluble species **15**·$(H_2O)_6$ was formed and successfully converted to its permethylated derivative **20**. Extension of this research will proceed in several directions. The scope of the reaction of **15** with alternative triflic acid esters[28] will be investigated to determine whether ether-functionalized sulfonate diester analogues of **15**[25a] can be obtained. Additionally, the analogous alkylation of **14**[25b] will be examined. An attractive long-term goal is the synthesis of a thiol species such as *closo*-1,12-$(HS)_2$-1,12-$C_2B_{10}(OR)_{10}$ and *closo*-1-H-12-HS-1,12-$C_2B_{10}(OR)_{10}$ (R = alkyl, aryl) via the reduction of the SO_3R-functions. Such compounds could play an important role in closomer chemistry.[5,6] Furthermore, sulfonic acid groups in **14**[25b] and **15**[25] will be replaced by alternative substituents such as phosphonate functions with the expectation of obtaining less hazardous intermediates.

Experimental Section

Caution! *On the scale and under the conditions described here, no explosions have occurred during the synthesis of the B-decahydroxylated compounds. Nevertheless, this does not rule out the possibility of such an event when dealing with carboranes and hydrogen peroxide. Departure from the reported procedures is not recommended, and extreme precautions should always be taken to ensure the identity and purity of all reagents and the use of adequate shielding to contain possible explosions.*

Caution! *The dry compounds closo-1,12-bis(sulfonic acid)-B-decahydroxy-p-carborane (**15**) and more severely closo-1-sulfonic acid-B-decahydroxy-p-carborane (**14**) are shock and heat sensitive. Extreme caution is advised when handling them. Mechanical and thermal stress should be avoided and protective apparel and suitable shielding must be employed.*

p-Carborane was purchased from Katchem Ltd., Czech Republic (http://www.katchem.cz) and Aldrich supplied the reagents *n*-BuLi, SO_2, SO_2Cl_2, anhydrous $AlCl_3$, $Ph_2(CH_3)SiCl$, $[(n\text{-}Bu)_4N]F$, and $CF_3SO_3\text{-}CH_3$. The H_2O_2 (30%), $Na_2CO_3{\cdot}H_2O$ (Fisher) was used as received. AG 500W-X8 (Bio-Rad) was used as the cation-exchange resin. The solvents THF and CH_2Cl_2 were dried over sodium metal and CaH_2, respectively, and distilled prior to use. All NMR spectra were recorded with Bruker ARX 400 and 500 spectrometers. Infrared spectra were obtained with a Nicolet Nexus 470 using KBr-pellets. Mass spectra (FAB) were obtained on a VG ZAB-SE mass spectrometer.

***closo*-1,12-Bis(sulfinic acid)-1,12-dicarbadodecaborane(12) (13).** A solution of *n*-BuLi in hexanes (5.9 mL, 13.9 mmol, 2.34 M) was added dropwise to a solution of *p*-carborane (1.0 g, 6.9 mmol) in THF at 0 °C. After the suspension had stirred for 2 h at ambient temperature, SO_2 (1.0 g, 15.6 mmol) was condensed in the reaction mixture at −78 °C. The reaction mixture was allowed to warm to room temperature and all volatiles were thoroughly removed under reduced pressure. The remaining off-white solid was washed with ether and dried to yield **10,** which was redissolved in H_2O (5 mL), filtered through a syringe filter (0.45 μm), and proton exchanged. The eluate was dried in vacuo and the remaining solid was recrystallized from CH_3CN to yield **13** as colorless crystals (1.65 g, 88%). Mp 208 °C. FT-IR (cm^{-1}): 3432 (br), 2627, 2441, 1792, 1322, 1080, 915, 875, 788, 732, 491, 442. ^{1}H NMR (400 MHz, [d_6]-acetone): δ 9.92 (2H, SO_2H), 3.5−1.6 (10H, BH).^{13}C NMR (100 MHz, [d_6]-acetone): δ 98.7 ($C_{carborane}$). ^{11}B{H} NMR (160.5 MHz, acetone): δ 15.8 (d, J = 153 Hz). MS (FAB, negative mode): 271.05 ($M - H^+$).

***closo*-1,12-Bis(chlorosulfonyl)-1,12-dicarbadodecaborane(12) (11).** Neat SO_2Cl_2 (1.2 g, 9.0 mmol) was added to a suspension of *closo*-1,12-bis(lithiosulfinato)-1,12-dicarbadodecaborane(12) (**10**) (see preparation of **13** above) (1.2 g, 4.2 mmol) in CH_2Cl_2 (30 mL) at 0 °C. All volatiles were removed under reduced pressure after the reaction mixture had stirred for 1 h at room temperature. Water was added to the remaining residue and the product was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with water and dried, and the residue was recrystallized (CH_2Cl_2) to yield **11** as colorless crystals (1.35 g, 94%). Mp 232 °C (lit.[11] mp 182 °C). FT-IR (cm^{-1}): 2650, 1394, 1182, 1085, 1026, 920, 777, 606, 563, 542. ^{1}H NMR (500 MHz, $CDCl_3$, 322K): δ 3.6−2.2 (BH).^{13}C NMR (125.8 MHz, $CDCl_3$, 322 K): δ 99.1 ($C_{carborane}$).^{11}B{H} NMR (160.5 MHz, CH_2Cl_2): δ −12.4 (d, J = 147 Hz). HR-MS (EI): calcd 341.0382, found 341.0378.

***closo*-1,12-Bis(sulfonic acid)-1,12-dicarbadodecaborane(12) (12).** A mixture of **11** (1.2 g, 3.5 mmol) and $AlCl_3$ (1.0 g, 7.5 mmol) in toluene (30 mL) was heated for 5 h at 85 °C. The toluene was distilled off and, at 0 °C, first water (30 mL) and then concentrated HCl (10 mL) were added to the residue. The mixture was filtered and dried under reduced pressure. The remaining solid residue was redissolved in water (5 mL), filtered through a syringe filter (0.45 μm), and proton exchanged. The dried eluate was recrystallized from Et_2O to yield **12** as colorless crystals (980 mg, 92%). Mp 219 °C. FT-IR (cm^{-1}): 3448, 2784, 2632, 2391, 1792, 1295, 1079, 915, 853, 794, 738, 601, 438. ^{1}H NMR (500 MHz, D_2O): δ 2.65−1.35 (BH).^{13}C NMR (125.8 MHz, D_2O, 10% CD_3OD): δ 101.7 ($C_{carborane}$).^{11}B{H} NMR (160.5 MHz, H_2O): δ −14.7 (d, J = 150 Hz). MS (FAB, negative mode): 304.11 ($M - H^+$, 15%), 287.09 ($M - H^+ - [OH]$, 45%), 287.09 ($M - H^+ - 2[OH]$, 45%), 223.08 ($M - H^+ - [SO_3H]$, 20%), 207.09 ($M - H^+ - [SO_3H] - [OH]$, 100%).

***closo*-1-Diphenylmethylsilyl-1,12-dicarbadodecaborane(12) (16).** A solution of *n*-BuLi in hexanes (6.3 mL, 13.9 mmol, 2.2 M) was added dropwise to a solution of *p*-carborane (2.0 g, 13.9 mmol) in THF at 0 °C and the reaction mixture was stirred at room temperature for 2 h. Upon addition of solid $Ph_2MeSiCl$ (3.23 g, 13.9 mmol) at −18 °C the reaction mixture was stirred at ambient temperature for 12 h. The solvent was removed under reduced pressure and unreacted *p*-carborane was sublimed with use of a dry ice cooled coldfinger. The sublimation residue was dissolved in toluene (80 mL) and extracted with water. The toluene was distilled from the organic phase and the dry residue was extracted with Et_2O (10 × 20 mL) leaving pure *closo*-1,12-bis(diphenylmethylsilyl)-*p*-carborane (**21**) as an undissolved solid. Compound **16** was sublimed from the residue of the dried Et_2O extract at 130 °C/10^{-5} Torr (2.5 g, 53%). Mp 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (4H, m, Ph), 7.42 (6H, m, Ph), 2.83 (1H, s, $C_{carborane}$−H), 3.00−1.55 (10H, BH), 0.68 (3H, s, CH_3).^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.5 (Ph), 132.7 (Ph), 130.9 (Ph), 128.0 (Ph), 73.6 ($C_{carborane}$), 67.8 ($C_{carborane}$), −3.0 ($SiCH_3$).^{11}B{H} NMR (160.5 MHz, benzene): δ (d, J = Hz). **21**: Mp 200 °C. ^{1}H NMR (500 MHz, [d_8]-toluene, 350 K): δ 7.52 (8H, m, Ph), 7.10 (12H, m, Ph), 3.00−1.85 (10H, BH), 0.50 (3H, s, CH_3).^{13}C NMR (125.8 MHz, [d_8]-toluene, 350 K): δ 137.6 (Ph), 135.9 (Ph), 134.2 (Ph), 130.2 (Ph), 79.3 ($C_{carborane}$), −2.9 ($SiCH_3$).^{29}Si NMR (99.4 MHz, [d_8]-toluene, 350 K): δ 9.42. ^{11}B-{H} NMR (160.5 MHz, toluene): δ −9.3 (d, J = 150 Hz).

***closo*-1-Sulfinic Acid-1,12-dicarbadodecaborane(12) (17).** A solution of *n*-BuLi in hexanes (2.67 mL, 5.9 mmol, 2.2 M) was added to a solution of **16** (2.0 g, 5.9 mmol) in THF at 0 °C. After the suspension had stirred for 2 h at ambient temperature, excess SO_2 was condensed in the reaction mixture at −78 °C. The reaction mixture was allowed to warm to room temperature and all volatiles were removed under reduced pressure. The remaining residue was resuspended in THF (20 mL) and a solution of $[(n\text{-}Bu)_4N]F$ in THF (6.5 mL, 6.5 mmol, 1 M) was added. The resulting clear solution was stirred at 50 °C for 8 h whereupon all volatiles were removed in vacuo. The resulting residue was redissolved in Et_2O (30 mL) and after extraction with H_2O (2 × 20 mL) flashed through a bed of silica with Et_2O. The silica was eluted with methanol and the eluate dried in vacuo. The obtained oily residue was proton exchanged with methanol/H_2O (1:4) and the solid residue obtained upon removal of the solvents in vacuo was recrystallized from

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CH_3CN to yield **17** as colorless crystals (787 mg, 64%). Mp 76 °C. FT-IR (cm^{-1}): 3335 (br), 2615, 1772, 1280, 1141, 1088, 1000, 906, 881, 838, 771, 726, 646, 589. ^1H NMR (500 MHz, [d_6]-acetone): δ 9.94 (s, SO_2H), 3.54 (1H, s, CH), 2.90−1.55 (10H, BH).^{13}C NMR (125.8 MHz, [d_6]-acetone): δ 98.5 ($C_{carborane}$), 63.7 ($C_{carborane}$).$^{11}B\{H\}$ NMR (160.5 MHz, acetone): δ −12.5 (d, J = 156 Hz). MS (FAB, negative mode): 207.11 (M − H^+, 100%), 223.10 (M + [O] + H^+, 85%).

***closo*-2,3,4,5,6,7,8,9,10,11-Decahydroxy-1,12-bis(sulfonic acid)-1,-12-dicarbadodecaborane(12) (15) and *closo*-2,3,4,5,6,7,8,9,10,11-Decahydroxy-1-sulfonic Acid-1,12-dicarbadodecaborane(12) (14).** Aqueous 30% H_2O_2 (30 mL) was added to either of the diacids **12** and **13** (3.5 mmol), which were placed in a 100 mL single-neck flask equipped with a reflux condenser seated in a Teflon sleeve. The solution was refluxed for 5 h, after which time samples were taken for ^{11}B NMR monitoring. For this purpose the reaction mixture was cooled to room temperature and then refluxed for a longer period, if required. Upon completion of the oxidation, concentrated HBr (20 mL) was added to the mixture and after being stirred for 2 h at room temperature the mixture was kept at 80 °C for 8 h. Evolving bromine was occasionally removed by a gentle steam of nitrogen. A negative KI/Starch test of a dried specimen indicates completion of the redox process. Thereafter, all volatiles were removed in vacuo and the remaining residue was triturated in methanol. The suspension was centrifuged and the supernatant solution was separated by using a pipet to withdraw the supernatant. This procedure was repeated five times. The extraction residue was dissolved in water, filtered, and dried to afford **14** as a colorless solid. *The dry compound can detonate when scratched and for the purpose of storage and transfer, stock solutions of it in H_2O are recommended.* Diacid **15** was obtained as colorless crystals from the methanol washings by slow evaporation.[18] **15**: Mp 230 °C (explosive dec). FT-IR (cm^{-1}): 3480 (br), 3220 (br), 2399 (br), 1642, 1300 (br), 1153 (br), 1049, 968, 734, 704, 630, 600, 535. ^{13}C NMR (125.8 MHz, CD_3OD): δ 62.0 ($C_{carborane}$). $^{11}B\{H\}$ NMR (160.5 MHz, MeOH): δ −16.0 (s). Negative-FAB: 462.91 (100%, M − H^+), 382.97 (40%, M − SO_3H^+). **14**: Mp 325 °C (explosive dec). FT-IR (cm^{-1}): 3268 (br), 2450 (br), 1645, 1306 (br), 1290 (br), 1044, 704, 618, 608, 533.^1H NMR (500 MHz, D_2O): δ 2.77 (s, CH). ^{13}C NMR (125.8 MHz, D_2O, 10% CD_3OD): δ 59.9 ($C_{carborane}$), 48.1 ($C_{carborane}$). $^{11}B\{H\}$ NMR (160.5 MHz, H_2O): δ −13.9 (s), −14.8 (s). MS (FAB, negative mode): 462.91 (100%, M − H^+), 382.97 (40%, M − SO_3H^+).

***closo*-2,3,4,5,6,7,8,9,10,11-Decahydroxy-1-sulfonic Acid-1,12-Dicarbadodecaborane(12) (14).** An aqueous solution of 30% H_2O_2 (20 mL) was added to freshly prepared *p*-carborane-1-sulfinic acid (**17**) (500 mg, 2.4 mmol) placed in a 100 mL single neck flask. Instantly a slightly exothermic reaction of brief duration occurred. The solution was refluxed for 3.5 h and the ^{11}B NMR monitored from this point on. After workup according to the previous protocol, **14** was obtained as a colorless powder. *The dry compound can detonate when scratched and for the purpose of storage and transfer, stock solutions of it in H_2O are recommended.* Yield 812 mg (88%).

***closo*-2,3,4,5,6,7,8,9,10,11-Decamethoxy-1,12-bis(sulfonic acid methyl ester)-1,12-dicarbadodecaborane(12) (20).** A mixture of the tetrahydrate of **15** (100 mg, 0.2 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (493 mg, 2.4 mmol), and methyl triflate (5 mL, 44.2 mmol) was heated to reflux for 5 h. All volatiles were removed under reduced pressure. The remaining residue was dissolved in CH_2Cl_2 and an aqueous solution of Na_2CO_3 monohydrate (325 mg, 2.62 mmol) was added dropwise. The organic layer was separated, washed with H_2O (2 × 15 mL), and dried over Na_2SO_4. After the solvent was removed in vacuo, the pyridine was sublimed at 50 °C (0.1 mm) with use of a dry ice cooled coldfinger. The remaining off-white solid was recrystallized from acetone/Et_2O to give **20** as colorless crystals (101 mg, 80%). Mp 320−325 °C dec. FT-IR (cm^{-1}): 2950, 2855, 1461, 1384, 1284, 1185, 1004, 967, 781, 577. ^1H NMR (500 MHz, [d_6]-acetone): δ 4.11 (6H, s, $SOCH_3$), 3.82 (30H, s, $BOCH_3$).^{13}C NMR (125.8 MHz, [d_6]-acetone): δ 67.8 (br, s, $C_{carborane}$), 59.8 (s, $SOCH_3$), 54.8 (s, $BOCH_3$). $^{11}B\{H\}$ NMR (160.5 MHz, acetone): δ −14.3 (s). HR-MS (EI): calcd 632.2446 and 633.2420, obsd 632.2457 and 633.2428.

X-ray Crystallography. All atoms were located by use of statistical methods. All non-hydrogen atoms were included with anisotropic displacement parameters. For **15**, **18**, and **19**, position parameters for all hydrogen atoms were refined. All hydrogen atoms for **20** were kept in calculated positions. The isotropic displacement parameters for hydrogen atoms were based on the values for the attached atoms. Scattering factors for H were obtained from Stewart et al.[29] and for other atoms were taken from.[30]

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Supporting Information Available: Tables listing atomic coordinates, temperature factors, bond lengths and angles, and torsion angles and details of the refinement of the X-ray crystallographic data (PDF); crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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