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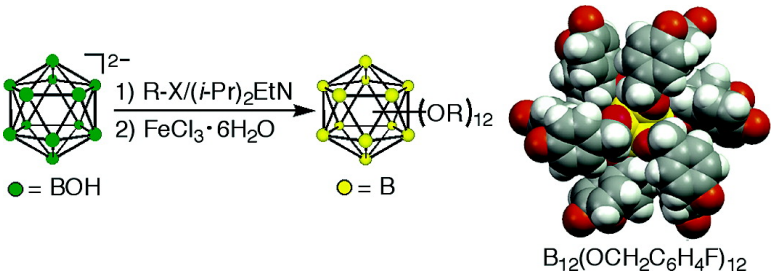

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Synthesis of Stable Dodecaalkoxy Derivatives of *hypercloso*-$B_{12}H_{12}$

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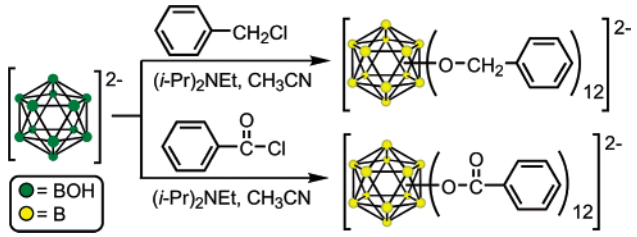
Abstract: The scope and limitations of the alkylation of [*closo*-$B_{12}(OH)_{12}]^{2-}$ using a series of fourteen alkyl and aralkyl halides and two *p*-toluenesulfonic acid esters in the presence of *N*,*N*-diisopropylethylamine have been investigated. The dodecaalkoxy-*closo*-dodecaborate products, [*closo*-$B_{12}(OR)_{12}]^{2-}$, and their *hypercloso* two-electron oxidation products have been explored. The species [*closo*-$B_{12}(OR)_{12}]^{2-}$ containing 26 cage-bonding electrons may undergo two reversible, sequential, one-electron oxidation processes, producing a 25-electron radical anion and a 24-electron neutral species. Several oxidizing reagents were investigated for the chemical oxidation of [*closo*-$B_{12}(OR)_{12}]^{2-}$ and [*hypercloso*-$B_{12}(OR)_{12}]^{-}$ to [*hypercloso*-$B_{12}(OR)_{12}$]. Both $FeCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$ in 90/5/5 ethanol/acetonitrile/H_2O were found to be the reagents of choice. The reverse reaction leading from the neutral species to the radical anion and subsequently to the dianion was achieved using sodium borohydride in ethanol. A variety of alkoxyl derivatives have been synthesized by heating the reactants for extended periods of time in acetonitrile at the reflux temperature. The use of elevated reaction temperatures attained by employing moderate argon pressure (autoclave) over the reaction mixture led to drastic reductions in reaction times and increased efficiency. X-ray diffraction studies of substituted dodecabenzyl ether derivatives proved that $\mathbf{2}^{2-}$ has approximate I_h symmetry while *hypercloso*-**2**, -**3**, -**9**, -**11**, -**12**, and -**13** have approximate D_{3d} point group symmetry due to Jahn−Teller distortion from I_h.

Introduction

Molecules with organic chains extending and branching from a rigid and compact spherical molecular platform have been attractive targets for synthesis and exploitation involving novel materials and biosciences applications. A potential platform precursor that may fulfill these requirements and potentially furnish a redox-active core is the icosahedral [*closo*-$B_{12}H_{12}]^{2-}$ ion.[1] The fascinating dianionic *closo*-boranes are a widely studied class of polyhedral boron clusters. In the cases of [*closo*-$B_{12}H_{12}]^{-2}$ and [*closo*-$B_{10}H_{10}]^{-2}$, their high stability, delocalized bonding, and ease of electrophilic B−H substitution suggest their description as three-dimensional species[2] not unlike aromatic hydrocarbons.

The discovery of the BH hydroxylation reaction leading to a variety of polyhedral borane and carborane structures such as [*closo*-$CHB_{11}(OH)_{11}]^{-}$ and [*closo*-1,12-$C_2H_2B_{10}(OH)_{10}$] and most often exemplified by the conversion of [*closo*-$B_{12}H_{12}]^{-2}$ to [*closo*-$B_{12}(OH)_{12}]^{-2}$, **1**, has revealed a new dimension in the chemistry of polyfunctional and redundantly substituted small molecules.[3−10] This is possible due to the facile derivatization of the B−OH vertexes in essentially the same fashion as alcohols using reactions in which the oxygen center is a nucleophile which reacts without B−O bond-breaking. Thus, 12-fold carboxylate ester[8,10] and ether[9] derivatives, now defined as closomers,[8,11] are available, and improved synthesis routes leading to the latter derivatives are described here. Scheme 1

Scheme 1. Synthetic Routes to Ester and Ether Closomers[8,9]



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presents representative reactions leading to closomers previously reported[8,9] and expanded here as well as in an upcoming paper.[12]

As previously pointed out,[8−10] closomer derivatives of **1** share some of the same characteristics as dendrimers. The principal differences are the smaller size, greater rigidity (dendrimers are more loosely constructed while closomers of the same functionality are more rigidly configured since 12 chains simultaneously originate at the icosahedral surface in close proximity to each other), higher symmetry, monodispersity, and much more compact presentation of functional groups seen with closomer derivatives of **1** as compared to dendrimer structures having the same, or similar, 12-fold functionality. In addition, derivatives of **1** can be obtained in which **1** plays the role of a dendrimer core providing 12-fold reactivity in the first generation. However, the differences between the conventional dendrimer structure and the corresponding derivatives of **1** appeared to be sufficiently great as to warrant a distinction between the two in nomenclature. Consequently, the relatively small polyfunctional derivatives of **1** have been designated as "closomers" to emphasize these distinctions. This unofficial nomenclature scheme is described fully elsewhere.[8,11]

As will be shown in detail in an upcoming paper,[13] the ether-linked closomers presented here have the unique property of undergoing facile and reversible one-electron redox reactions involving the parent closomer B_{12}^{2-} core structure. Thus, species containing the B_{12}^{2-} (26 electrons), B_{12}^{-} (25 electrons), and neutral B_{12} (24 electrons) core structures are easily interconverted using chemical or electrochemical redox reactions. The two one-electron redox processes of **2** belonging to the $\{[B_{12}(OBn)_{12}]^{2-}/\{[B_{12}(OBn)_{12}]^{1-}\}$ and $\{[B_{12}(OBn)_{12}]^{1-}/\{[B_{12}(OBn)_{12}]\}$ couples have $E_{1/2}$ values of 0.06 and 0.56 V versus AgCl, respectively. The 24- and 25-electron species are stabilized by back-bonding to the electron-deficient B_{12} core by nonbonding electrons available on each of the 12 ether oxygen substituents. X-ray diffraction studies using the dodecabenzyl ether system proved that $\mathbf{2}^{2-}$ and $\mathbf{2}^{1-}$ have approximate I_h symmetry while **2** exhibits approximate D_{3d} symmetry due to Jahn−Teller distortion.[9] The ORTEP structures of $\mathbf{2}^{2-}$ and **2**, along with representative B−B and B−O bond lengths observed in **2**, are presented in Figures 1 and 2 and Table 2, respectively. The B−B distances designated as a six-pointed star in the structure of **2** (Figure 2) are long compared to comparable distances found in $\mathbf{2}^{2-}$, while B−O distances observed at these same B atoms are shortened relative to those observed in $\mathbf{2}^{2-}$. This shortening is attributed to back-bonding of nonbonding ether oxygen electrons with the electron-deficient D_{3d} cage. Therefore, the cages of $\mathbf{2}^{2-}$, $\mathbf{2}^{1-}$, and **2** have the property of a pseudometal center characterized by redox reactions and stabilization of electron-deficient oxidation states by back-bonding of substituent nonbonding electrons. Additionally, the crystal structures of **3** and **9** shown in Figure 3 and 4 exhibited approximate D_{3d} symmetry and confirmed the assignment of this point group to **2**.

Following the initial publications concerning closomer chemistry,[8,9] the application of density functional theory to anionic and neutral persubstituted 12-vertex boron cage systems was

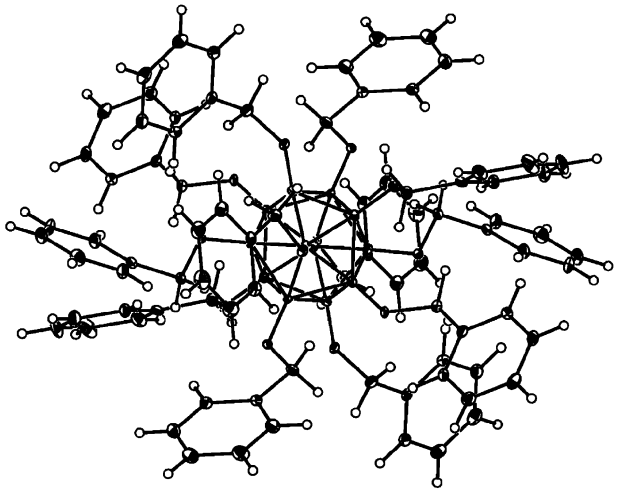

Figure 1. ORTEP diagram of dodeca(benzyloxy)dodecaborane dianion ($\mathbf{2}^{2-}$) having an approximate I_h symmetry.[9]

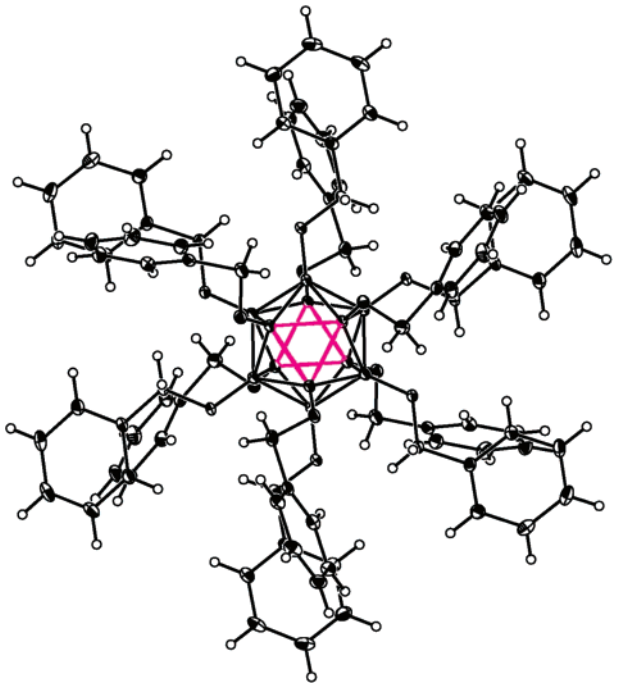

Figure 2. ORTEP diagram of dodeca(benzyloxy)dodecaborane (**2**) with distorted icosahedral (an approximate D_{3d}) symmetry.[9]

reported by McKee.[14] These results supported the existence of the two observed reversible one-electron oxidation reactions of the B_{12} core as well as the ^{11}B NMR chemical shifts of the dianion and neutral ether closomers. In addition, a ^{11}B downfield shift of 51.6 ppm is predicted on going from [*closo*-$B_{12}(OR)_{12}]^{2-}$ to [*hypercloso*-$B_{12}(OR)_{12}$]. This is in excellent agreement with the experimental values of 54−58 ppm observed throughout this study. The DFT description of **2** at the AM1 level predicted a T_h structure to be 13.2 kcal/mol more stable than a D_{3d} structure. Conversely, Fujimori and Kimura[15] predicted from energy minimization computations carried out at the HF/6-31G(d) level for *hypercloso*-$B_{12}H_{12}$ that an undistorted icosahedral structure would have partially occupied 4-fold degenerate

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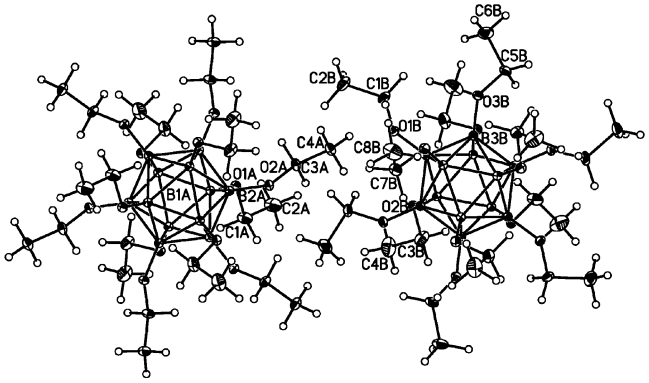

Figure 3. ORTEP diagram of the structure of dodecaethoxy-*hypercloso*-dodecaborane (**3**) crystallized from methanol.

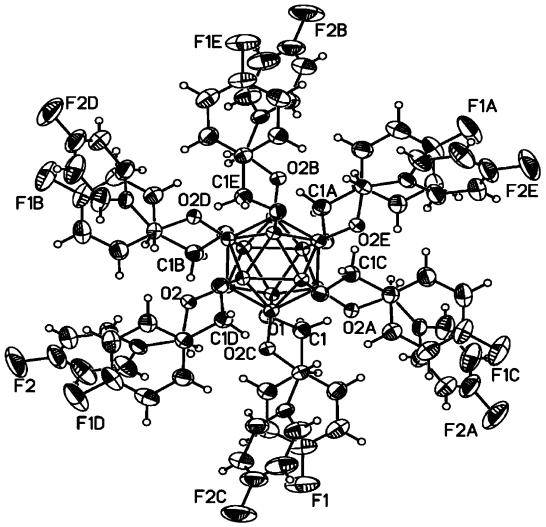

Figure 4. ORTEP diagram of the structure of dodeca(4-fluorobenzyloxy)-*hypercloso*-dodecaborane (**9**) crystallized from toluene.

HOMOs, and a Jahn−Teller distortion to D_{3d} symmetry was predicted.

Other examples of icosahedral borane derivatives which violate Wade's $2n + 2$ electron-counting rule[16] (n = number of vertexes) are [*hypercloso*-$B_{12}(CH_3)_{12}]^-$,[17] [*hypercloso*-$CB_{11}(CH_3)_{12}]$,[18] and *hypercloso*-B_xCl_x ($x = 4, 7-12$).[19] The unusual electron count can be stabilized by the *exo*-halogen substituents which supply additional electron density to the cage through π-back-bonding of nonbonded electrons or through hyperconjugation between the methyl substituents and cage.[18] Steric protection and electron donation from the substituents (ether oxygen) are responsible for the unusual stability of the ether closomers. Novel closomers based upon carboxylate ester structures,[8,10] which are not capable of *hypercloso* cage stabilization, will be presented in an upcoming paper.[12]

While applications of redox-active ether-linked closomers have not been fully developed at this time, in this paper and an upcoming paper,[13] it is suggested that they may find applications including molecular electronics,[20] electrocatalysis,[21] information storage,[22] components in drug delivery systems,[23,24] fluorophores,[25] radionuclide chelators,[26−29] and other biomedical applications.[30−39] Dendrimers have been employed in many of these applications; their syntheses by either convergent[40] or divergent[41] pathways can be difficult to control, resulting in polydispersity. In this paper we expand upon the original paper[9] and further describe the synthesis, purification, and characterization of monodispersed ether-linked closomers.

Results and Discussion

The original paper on ether-linked closomers[9] was accompanied by a paper describing closomers linked by carboxylate ester bonds.[8] An additional brief paper described a nanoparticle created for use as a boron neutron capture therapy agent comprised of 12 [*nido*-7,8-$C_2B_9H_{11}]^-$ anions attached through carboxylate ester spacer groups to an icosahedral B_{12}^{2-} core.[10] Recent advances in ester closomers will be forthcoming in a separate paper.[12]

Since the original publication of this work,[9] the hydroxylation of Cs_2[*closo*-$B_{12}H_{12}$] to produce Cs_2-**1** has been markedly improved to give yields of 95% or greater.[4] Although previously predicted to be unstable,[14] Cs_2-**1** exhibited remarkable thermal stability as heating for 2 days at 200 °C in acetonitrile gave no evidence of decomposition. This work rests upon the earlier sequential hydroxylation of Cs_2[*closo*-$B_{12}H_{12}$] with aqueous H_2SO_4 to produce, at will, a single isomer of Cs_2[*closo*-$B_{12}H_{12-n}(OH)_n$] ($n = 1-4$ inclusive).[42,43] The latter species were subsequently explored in unpublished reactions with electrophilic reagents such as alkyl halides, acyl chlorides, alkanesulfonyl chlorides, phenyl isocyanate, and titanocene dichloride, and they may serve as precursors for more complex structures.

Alkylation of [*closo*-$B_{12}(OH)_{12}]^{2-}$. A new and improved method for the synthesis and isolation of ether-linked closomers has been established by the alkylation of $(TBA)_2$-**1** [TBA =

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Table 1. Methods and Conditions Employed for Ether Closomer Synthesis

closomer ether	R in $(BOR)_{12}$	method/ reagent[a]	reaction time/ temp	yield[b] (%)
2	benzyl	1/benzyl bromide	6 d/reflux	69
		2/benzyl chloride	4 h/150 °C	65
3	ethyl	2/bromoethane	12 h/150 °C	70
4	hexyl	1/1-bromohexane	23 d/reflux	80
		2/1-bromohexane	8 h/150 °C	75
		2/*n*-hexyl tosylate	2 h/150 °C	70
5	pentyl	1/1-bromopentane	21 d/reflux	78
		2/1-bromopentane	7 h/150 °C	75
6	allyl	1/allyl bromide	7 d/reflux	55
		2/allyl chloride	3 h /150 °C	60
7	3-butenyl	1/4-bromo-1-butene	19 d/reflux	65
		2/4-bromo-1-butene	6 h/150 °C	62
8	3-methyl-1-butyl	2/1-(bromomethyl)butane	8 h /150 °C	75
9	4-fluorobenzyl	1/4-fluorobenzyl bromide	5 d/reflux	59
		2/4-fluorobenzyl chloride	1 h/150 °C	68
10	methyl	2/methyl tosylate	2 h/150 °C	50
11	3-fluorobenzyl	2/3-fluorobenzyl chloride	4 h/150 °C	60
12	4-chlorobenzyl	2/4-chlorobenzyl chloride	5 h/150 °C	75
13	4-bromobenzyl	2/4-bromobenzyl bromide	5 h/150 °C	70
14	3-bromobenzyl	2/3-bromobenzyl bromide	5 h/150 °C	65
15	4-methylbenzyl	2/4-methylbenzyl chloride	5 h/150 °C	55
16	4-methoxybenzyl	2/4-methoxybenzyl chloride	1 h/150 °C	30

[a] Acetonitrile was used in all reactions. [b] Isolated yield of $B_{12}(OR)_{12}$ based on $(TBA)_2$-**1**.

Table 2. Selected Bond Lengths (Å) of **2**, **3a**, **3b**, **9**, **12**, and **13** Based on Figure 5

closomer	BA–OA	BB–OB	CA–OA	CB–OB	BA–BA	BB–BB
2	1.369(2)	1.398(2)	1.440(2)	1.433(2)	1.808(2)	1.862(2)
	1.377(2)	1.403(2)	1.442(2)	1.437(2)	1.911(2)	1.862(2)
	1.378(2)	1.404(2)	1.446(2)	1.441(2)	1.918(2)	1.864(2)
3a	1.394(2)	1.384(2)	1.431(2)	1.858(3)	1.858(3)	1.864(2)
3b	1.389(3)	1.388(2)	1.432(2)	1.860(3)	1.860(3)	1.867(2)
	1.391(2)	1.388(2)	1.433(2)	1.869(3)	1.869(3)	1.868(2)
9	1.354(4)	1.388(2)	1.431(2)	1.914(5)	1.914(5)	1.866(2)
						1.867(2)
12	1.375(3)	1.365(4)	1.408(3)	1.748(4)	1.748(4)	1.755(4)
	1.386(3)	1.377(3)	1.417(3)	1.851(4)	1.851(4)	1.848(4)
	1.389(3)	1.401(4)	1.437(3)	1.898(4)	1.898(4)	1.873(4)
13	1.364(6)	1.365(4)	1.409(6)	1.768(7)	1.768(7)	1.763(7)
	1.383(6)	1.371(6)	1.415(6)	1.858(7)	1.858(7)	1.844(7)
	1.387(6)	1.385(6)	1.437(6)	1.910(7)	1.910(7)	1.928(7)

tetra-*n*-butylammonium]. The TBA salt of **1** was chosen due to its enhanced solubility in such organic solvents as dichloromethane and acetonitrile, when compared with its alkali-metal salt counterparts. Moreover, the traditional use of K_2CO_3 as a base in the synthesis of polyether dendrimers[40] is totally ineffective here due to the extremely low solubility of the potassium salt of **1** in organic solvents. Therefore, *N*,*N*-diisopropylethylamine was employed as the base of choice for closomer syntheses.

As previously reported,[9] the reaction of $(TBA)_2$-**1** with excess benzyl chloride and *N*,*N*-diisopropylethylamine in acetonitrile solvent at the reflux temperature (method 1) produced structurally characterized closomers having 12 benzyl ether groups and the ability to undergo sequential redox reactions. In Table 1, we report improved methods for the synthesis and purification of a wide variety of alkyl and aralkyl ether closomers. An alternative synthetic method (method 2) involved heating reaction mixtures under moderate argon pressure in an autoclave to attain elevated reaction temperatures, thereby drastically reducing the time required for complete reaction when compared to reactions carried out at the normal acetonitrile reflux temperature. In these studies identical reaction mixtures were studied under both sets of conditions. A temperature of 150 °C and pressures ranging from 500 to 1500 psi were arbitrarily employed. Under these conditions, the reaction time was reduced from many days to a few hours while good reaction yields were maintained, demonstrating this procedure to be the method of choice for the ether-linked closomer synthesis.

Scheme 2. An Ether Closomer Side Reaction Leading to Closomer Oxidation and Radical Formation Where R = Benzyl

$$[B_{12}(OR)_{12}]^{2-} + RX \longrightarrow [B_{12}(OR)_{12}]^{-} + R\bullet + X^{-}$$

$$2R\bullet \longrightarrow R\text{-}R$$

The previously described alkylation conditions (method 1) were successfully applied to fourteen organic halides and two *p*-toluenesulfonate esters. A 120-fold mole ratio of starting reagent to $(TBA)_2$-**1** is essential for complete reaction in acetonitrile at the reflux temperature and atmospheric pressure. When the temperature was increased to 150 °C at elevated pressure, the initial concentration of excess reagent was reduced to an 18-fold mole ratio relative to that of $(TBA)_2$-**1** while the reaction time was similarly reduced. As an example, allyl chloride was chosen for the study of reaction time with respect to initial reagent concentration. The reaction times obtained with different initial concentrations of allyl chloride versus constant $(TBA)_2$-**1** were determined at 150 °C. Completion of the reaction was determined by employing ^{11}B NMR spectra initially observed as a symmetrical singlet near −18 ppm corresponding to $(TBA)_2$-**1** and subsequently coalescing to a symmetrical singlet near −16 ppm associated with $[closo\text{-}B_{12}(OR)_{12}]^{2-}$. The results showed that the necessary time for complete reaction decreased with increasing initial allyl chloride concentration, and the reaction was complete in 45 h when the initial excess reagent was reduced to a 24-fold mole ratio relative to $(TBA)_2$-**1**.

Alternative precursors for the synthesis of the ether-linked closomers are *p*-toluenesulfonate esters. Fortunately, for reactions in which the desired organic halides are too volatile to be conveniently handled (such as CH_3Br) or the corresponding alcohols are readily available, the corresponding *p*-toluenesulfonates can be utilized as convenient reagents. Thus, *p*-toluenesulfonate esters have proven to be outstanding precursors for closomer etherification reactions.

Oxidation of $[closo\text{-}B_{12}(OR)_{12}]^{2-}$. In principle, the *N*,*N*-diisopropylethylammonium ion byproduct generated during the etherification reaction can compete with the tetrabutylammonium ion as the counterion for the dianionic ether closomer product. In addition, $B_{12}(OR)_{12}^{-}$ is generated during the alkylation reaction through accidental oxygen contamination (these closomers can be easily air oxidized to the anion radical) and/or reaction with excess benzyl halide as shown in Scheme 2. Evidence of such radical formation is the observation of bibenzyl in the mass spectrum of the crude reaction product. These side reactions result in the formation of mixed salts and oxidation states of the closomer ion which complicate product isolation. To facilitate product isolation and purification, oxidation of the crude reaction product to the uncharged *hypercloso* closomer was followed by its purification using chromatography.

A variety of oxidants and reaction conditions were investigated in the representative synthesis of dodeca(allyloxy)-*hypercloso*-dodecaborane, such as O_2, H_2O_2, Br_2, I_2, $H_2Cr_2O_7$,

Table 3. Distances (Å) between the Most Distant Antipodal Atom Pairs

closomer	antipodal–outermost atom (on phenyl ring)	ligand bonded to BA	ligand bonded to BB
2	phenyl carbon−phenyl carbon	15.703(5), 15.728(4), 15.742(4)	15.858(5), 15.898(6), 15.927(5)
3a	methyl carbon−methyl carbon	10.487(4)	10.743(3)
3b	methyl carbon−methyl carbon	10.730(3)	10.597(3)
9	fluorine−fluorine	17.194(5)	18.486(3)
11	fluorine−fluorine	15.339(9), 17.501(7), 17.856(6)	15.952(6), 16.955(5), 17.523(6)
12	chlorine−chlorine	19.496(3), 19.377(2), 19.572(3)	17.850(2), 18.001(3), 18.162(2)
13	bromine−bromine	19.816(2), 19.696(2), 19.855(2)	18.154(2), 18.434(2), 18.383(2)
14	bromine−bromine	14.402(2), 15.991(2), 18.255(2)	17.791(2), 17.980(2), 18.128(2)

$KMnO_4$, MnO_2, $HgCl_2$, $Pd(OAc)_2$, $PdCl_2$, $Ag(NO_3)_2$, $Ag(OAc)_2$, $CuSO_4$, $CuCl_2$, $Fe_2(SO_4)_3.nH_2O$, $FeCl_3$, $FeCl_3{\cdot}6H_2O$, $K_3Fe(CN)_6$, $Fe(NO_3)_3$, and tetrachloro-1,4-benzoquinone. As determined from ^{11}B NMR spectra, the best results were obtained with Fe(III) in 90/5/5 ethanol/acetonitrile/H_2O at room temperature. The remaining oxidants (such as $H_2Cr_2O_7$) either totally oxidized the borane cage to boric acid or failed to react. A possible explanation of these results is that the Lewis acidity of Fe(III) facilitates the oxidation pathway by coordinating to the ether oxygen centers via the nonbonding electron pairs.[44,45] The preparative yield of the neutral *hypercloso* compounds using Fe(III) in 90/5/5 ethanol/acetonitrile//H_2O generally ranged from 30% to 80% (yield of $B_{12}(OR)_{12}$ based on $(TBA)_2$**1)**.

All of the neutral 24-electron compounds exhibit desirable properties, such as extreme solubility in common organic solvents (e.g., hexane, benzene, dichloromethane, diethyl ether, acetonitrile, and ethyl acetate), air stability over extended periods of time, and thermal stability. In addition, the dodeca(allyloxy) and dodeca(4-butenoxy) derivatives, **6** and **7**, respectively, are particularly interesting since they contain 12 terminal carbon−carbon double bonds on the outer surface of the ether closomer, offering the potential opportunity for further functionalization.

X-ray Diffraction Studies. The solid-state structures of **3** and **9** determined by X-ray diffraction are illustrated in Figures 3 and 4. An undistorted icosahedral *hypercloso*-$[B_{12}H_{12}]$ structure would have partially occupied, 4-fold degenerate HOMOs, whose degeneracy can be removed by Jahn−Teller distortion. Recently, a distorted icosahedron with D_{3d} symmetry was identified as an energy minimum in computations carried out at the HF/6-31G(d) level for *hypercloso*-$[B_{12}H_{12}]$ by Fujimori and Kimura.[15] However, McKee predicted by density functional calculations that a T_h structure has lower energy than the observed D_{3d} symmetry structure for **2** and **3**[14] and concluded that secondary effects, such as crystal packing, were responsible for the disagreement. In fact, none of the seven neutral closomer X-ray structures obtained showed evidence of T_h symmetry.

The solid-state structures of **2**, **3**, **9**, **11**, **12**, **13**, and **14** have been determined by X-ray crystallography, with **3** exhibiting two types of symmetry, designated **3a** and **3b**. None of these molecules are true icosahedra, but all show evidence of crystallographic symmetry. Seven of eight types are centrosymmetric, with the only exception being one of the two types of **3**, **3a**, which contains only a 3-fold axis. The second type of molecule in **3**, **3b**, has a 3-fold axis and a center of symmetry, as does **9**. The remaining structures have only a center of symmetry. Selected bond distances for **2**, **3a**, **3b**, **9**, **12**, and **13** are listed in Table 2.

(44) (a) Streitwieser, A. *Chem. Rev.* **1956**, *56*, 571. (b) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1968. (c) King, J. F.; Tsang, G. T. Y. *J. Chem. Soc., Chem Commun.* **1979**, 1131.
(45) Ganem, B.; Small Jr., V. R. *J. Org. Chem.* **1974**, *39*, 3728.

Figure 5 illustrates a common structural core of the dodecaalkoxydodecaboranes consisting of the B_{12} framework and the oxygen atoms α- and the carbon atoms *β*- to the boron atoms. The variation of distance between the antipodal outermost atoms shown in Table 3 is an indication of the nonspherical nature of these closomers. This deviation from icosahedral symmetry results in an approximate 3-fold axis as in **2**, **11**, **12**, and **13** and a true 3-fold axis as in **3a**, **3b**, and **9,** while **14** exhibits no 3-fold axis. In a true icosahedron, all six distances between these antipodal pairs of atoms would be equal.

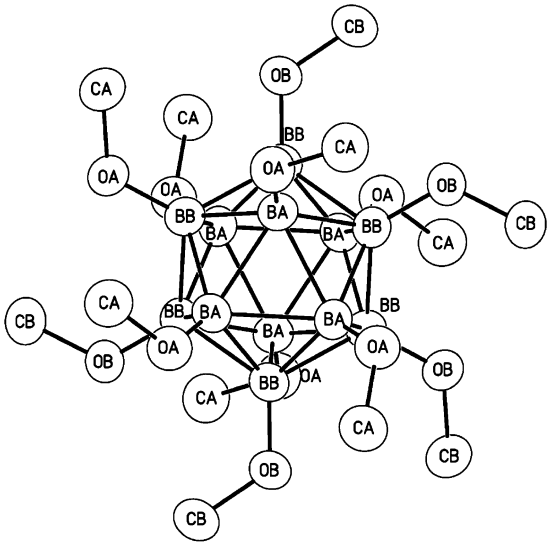

Figure 5. A model of a dodecaalkoxydodecaborane with a 3-fold axis and a center of symmetry.

Conclusions

Fifteen new dodecaalkoxy-*hypercloso*-dodecaborane derivatives of [*closo*-$B_{12}(OH)_{12}]^{2-}$, $B_{12}(OR)_{12}$, have been successfully prepared and purified by employing sequential *O*-alkylation followed by oxidation to the corresponding neutral *hypercloso* derivative and gel filtration with silica or alumina. A variety of alkyl and aralkyl halides, as well as *p*-toluenesulfonate esters, were employed to produce the ether-linked closomers in excellent yield. The closomer ether product, *closo*-$[B_{12}(OR)_{12}]^{2-}$, is oxidized to *hypercloso*-$[B_{12}(OR)_{12}]^{1-}$, which is further oxidized with Fe(III) to *hypercloso*-$B_{12}(OR)_{12}$ followed by isolation and characterization. Mass spectrometry and ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy were utilized to characterize the *hypercloso*-$B_{12}(OR)_{12}$ species. The reduction of the neutral species to the corresponding radical anion and subsequently to the dianion was achieved using sodium borohydride in ethanol. The described methodology also allows recovery of the unreacted aralkyl halide, alkyl halide, and *p*-toluenesulfonate starting materials. An X-ray diffraction study of **3**, **9**, **11**, **12**,

and **13** demonstrated that these neutral closomers have approximate D_{3d} symmetry as does **2**. All of the neutral closomers exhibit a shortening of the B−O bond, indicating an increase in double bond character as compared to a typical B−O single bond. π-Back-bonding and steric factors, among others, may be responsible for the stability of the *hypercloso*-$B_{12}(OR)_{12}$ species in these cases. The interesting oxidation−reduction properties of these compounds will be presented in an upcoming paper.[13]

Experimental Section

General Considerations. Both *N*,*N*-diisopropylethylamine and acetonitrile were freshly distilled from CaH_2 prior to use. All reactions were carried out under anhydrous, oxygen-free conditions (oven-dried glassware and argon). The organic halides and $FeCl_3 \cdot 6H_2O$ were purchased from Aldrich, Lancaster, and Fisher. Methyl and *n*-hexyl *p*-toluenesulfonate were purchased from Acros Organics and TCI America, respectively. All of the purchased chemicals were used without further purification. ^{11}B NMR spectroscopy (160 MHz) was performed on a Bruker ARX-500 spectrometer and referenced externally to $BF_3 \cdot Et_2O$. Bruker ARX-500, ARX-400, and Avance-500 spectrometers were used to obtain ^{13}C, ^{1}H, and ^{19}F spectra. Mass spectra were obtained using a high-resolution Ultima 7T. The autoclave utilized in pressurized reactions was an EZE-Seal manufactured by Autoclave Engineers, Inc.

Dicesium Dodecahydroxy-*closo*-dodecaborate (Cs_2-1). In a 250 mL Erlenmeyer flask, 50.0 g (237 mmol) of CsCl was dissolved in 40.0 mL of ion-free water. In a separate 250 mL Erlenmeyer flask, 20.0 g (90.9 mmol) of [*closo*- $K_2B_{12}H_{12}$] was dissolved in 50 mL of ion-free water. The [*closo*- $K_2B_{12}H_{12}$] solution was added slowly to the CsCl solution with vigorous stirring. The resulting milky suspension was chilled at −5 °C for 12 h. The white solid was separated by filtration and then recrystallized from hot ion-free water. The white crystals were separated by filtration, and the excess water was removed by employing a lyophilizer. The total yield was 53.4 g (98%) of pure Cs_2[*closo*-$B_{12}H_{12}$].

The synthesis of Cs_2[closo-$B_{12}(OH)_{12}$] from Cs_2[closo-$B_{12}H_{12}$] was performed as previously described.[3,4] *Precautions and careful planning should always be employed to ensure the identity and purity of the reagents. Adequate shielding is required to contain possible explosions. Under no circumstances must hydrogen peroxide come in contact with organic material or solvents due to the possibility of explosion.*

Di(TBA)-dodecahydroxy-*closo*-dodecaborate [$(TBA)_2$-1]. Ion-exchange resin (Bio Rad AG 50W-X8) was used to convert Cs_2-**1** to $(TBA)_2$-**1** as follows: In a 500 mL beaker, 200 mL of acid-form resin was washed with ion-free water until a pH of 7.00 was obtained. With stirring, 5 mL aliquots of 40% tetrabutylammonium hydroxide were added until the suspension reached a pH greater than 10. The resin was washed with ion-free water until neutral and then slurry-packed in a column (5 × 30 cm). The column was wrapped with heating tape, and the temperature was brought to 50 °C. A 10 g (16.7 mmol) portion of Cs_2-**1** was dissolved in 1 L of boiling ion-free water. The solution was then cooled to 50 °C and passed through the column, which was then washed with an additional 1 L of warm water. The water was removed using a rotary evaporator. The remaining traces of water were removed azeotropically using benzene or simply lyophilized to yield 12.5 g (92%) of pure $(TBA)_2$-**1**.

Alkylation of $(TBA)_2$-1 Using Alkyl and Aralkyl Halides: General Procedure Method 1. Under an argon atmosphere, in a 100 mL oven-dried Schlenk flask, 0.50 g (0.61 mmol) of $(TBA)_2$-**1** was dissolved in 25.0 mL of freshly distilled acetonitrile. Employing a syringe, 2.00 mL (11.5 mmol) of *N*,*N*-diisopropylethylamine and 76.0 mmol of alkyl halide or *p*-toluenesulfonate ester were added. The reaction mixture was heated at the reflux temperature. The progress of the etherification reactions was monitored using ^{11}B NMR spectra, starting as a symmetrical singlet near −18 ppm which corresponds to $(TBA)_2$-**1** and then progressing to an asymmetric peak which is characteristic of partial random substitution of the vertexes during the reaction. Final coalescence to a symmetrical singlet near −16 ppm corresponds to [*closo*-$B_{12}(OR)_{12}]^{2-}$, which is indicative of the completion of the reaction. The reaction mixture passed through different color stages, starting with yellow and continuing with orange and finally finishing as a light pink, dark purple, or blood red solution. When the reaction was complete, the volatiles were removed using a rotary evaporator. With the exception of **2**, **6**, **9**, **11**, **12**, **13**, **14**, and **16,** the remaining residue was dissolved in dichloromethane and chromatographed on neutral Al_2O_3 or silica. Yellow and pink/purple fractions were separated, and the solvent was removed from both fractions using a rotary evaporator. The ^{11}B NMR spectra of both fractions were obtained and revealed a resonance near 41 ppm corresponding to the yellow fraction, which consisted of the neutral compound *hypercloso*-$B_{12}(OR)_{12}$. The pink/purple fraction, which contained the charged species, displayed a resonance near −15 ppm.

The pink/purple fraction or the residue of **2**, **6**, or **9** was dissolved in 10.0 mL of 90/5/5 ethanol/acetonitrile/H_2O, 2.00 g of $FeCl_3 \cdot 6H_2O$ was added, and the resulting solution was stirred for 12 h at room temperature. The solvent was removed using a rotary evaporator. The remaining brown residue was dissolved in dichloromethane and chromatographed on neutral Al_2O_3 or silica. The yellow and pink/purple fractions were separated. The above procedure can be repeated on the recovered pink/purple fraction to accumulate additional *hypercloso*-$B_{12}(OR)_{12}$.

General Procedure Method 2. After the starting materials were mixed as described in method 1, the reaction mixture was then placed into a 100 mL autoclave equipped with a glass liner under argon. The reaction was carried out at 150 °C under elevated argon pressure until reaction completion. The reaction was monitored via ^{11}B NMR spectra, as described above. When the reaction was complete, the procedure described in method 1 was employed to isolate *hypercloso*-$B_{12}(OR)_{12}$.

Dodeca(benzyloxy)-*hypercloso*-dodecaborane (2). Method 1. The reaction mixture was refluxed for 6 d after addition of 8.70 mL (73.0 mmol) of benzyl bromide. *If the color of the reaction turns to yellow/brown, the reaction should be repeated while oxygen is carefully excluded.* The excess benzyl bromide was removed chromatographically by employing neutral alumina or silica. After elution with 35% EtOAc/65% hexanes and then CH_2Cl_2 to remove the excess starting material, the pink/purple product mixture was eluted with EtOAc. The purple residue was oxidized according to the general procedures and then chromatographed on silica by employing 35% EtOAc/65% hexanes to elute a yellow fraction (**2**), and the remaining purple fraction was eluted with EtOAc. The oily yellow **2** was crystallized from ethanol to give the yellow-orange solid in 69% yield.

Method 2. After addition of 8.40 mL (73.0 mmol) of benzyl chloride, the reaction was conducted at 150 °C and 800 psi for 4 h. When the reaction was complete, the procedure described above for method 1 was followed. The neutral closomer **2** was isolated in 65% yield.

Compound **2** is an orange solid (melting point 147.5−149.0 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.57 (s, 24 H), 7.02−7.28 (m, 60 H). ^{13}C NMR (125.5 MHz, $CDCl_3$): δ 73.1, 127.0, 128.1, 140.5. ^{11}B NMR (160 MHz, MeCN): δ 41.6. HRMS (MALDI): *m*/*z* calcd for $C_{84}H_{84}O_{12}B_{12}$ (M^-), 1415.7177; found, 1415.7247.

Dodecaethoxy-*hypercloso*-dodecaborane (3). Method 2. In a 100 mL oven-dried Schlenk flask, 0.50 g (0.61 mmol) of $(TBA)_2$-**1** was dissolved in 25.0 mL of freshly distilled CH_3CN, and the solution was chilled in an ice bath. Using a syringe, 2.00 mL (11.5 mmol) of *N*,*N*-diisopropylethylamine and 16.6 mL (222 mmol) of bromoethane were added. Under argon, the reaction mixture was transferred to a 100 mL glass-lined autoclave via syringe. The reaction was carried out at 150 °C and 1000 psi. The reaction reached completion after 12 h. The ^{11}B NMR spectrum of the completed reaction mixture showed two major peaks, one around 38 ppm characteristic of **3** and the second near −16 ppm indicating charged closomers. A yellow fraction was eluted with

CH_2Cl_2, and a purple fraction was eluted with EtOAc. Oxidation of the purple fraction was performed as described in the general procedure. The neutral closomer **3** was isolated in 70% yield.

Compound **3** is a dark-orange solid (sublimes at 168 °C, 1 atm). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, J = 7.0 Hz, 36 H), 4.08 (q, J = 7.0 Hz, 24 H). ^{13}C NMR (125.5 MHz, $CDCl_3$): δ 17.7, 66.7. ^{11}B NMR (160 MHz, MeCN): δ 37.3. HRMS (MALDI): *m*/*z* calcd for $C_{24}H_{60}O_{12}B_{12}$ (M^-), 670.5292; found, 670.5279.

Dodeca(*n*-hexoxy)-*hypercloso*-dodecaborane (4). Method 1. After addition of 9.00 mL (76.0 mmol) of 1-bromohexane, the reaction mixture was refluxed for a total of 23 d under argon as described in the general procedure. The ^{11}B NMR spectrum of the reaction mixture, starting from day 17, showed a small peak around 41 ppm characteristic of the neutral closomer in addition to the −15 ppm singlet originating from $\mathbf{4}^{2-}$. After completion of the reaction the excess 1-bromohexane was removed using a high vacuum with warming at 60 °C. The remaining red residue was chromatographed on neutral Al_2O_3 or silica. A yellow fraction was eluted with 20% CH_2Cl_2/80% hexanes, and a pink/purple fraction was eluted with EtOAc. Further oxidation of the purple fraction was performed as described in the general procedure. Closomer **4** was afforded in 80% yield.

Method 2. The reagents were combined as described in the general procedure. The reaction was carried out at 150 °C and 500 psi for 8 h. Isolation of **4** was performed as described above. The neutral closomer **4** was isolated in 75% yield.

The neutral closomer **4** is a dark yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.1 Hz, 36 H), 1.32 (m, 72 H), 1.54 (m, 24 H), 4.02 (t, J = 6.4 Hz, 24 H). ^{13}C NMR (125.5 MHz, C_6D_6): δ 13.9, 22.8, 26.0, 31.8, 32.4, 70.5. ^{11}B NMR (160 MHz, MeCN): δ 41.2. HRMS (MALDI): *m*/*z* calcd for $C_{72}H_{156}O_{12}B_{12}$ (M^-), 1344.2811; found, 1344.2834.

Dodeca(*n*-pentoxy)-*hypercloso*-dodecaborane (5). Method 1. After addition of 9.20 mL (74.0 mmol) of 1-bromopentane, the reaction mixture was refluxed for 21 d under argon. The ^{11}B NMR spectrum, starting from day 19, contained a small resonance near 41 ppm associated with the neutral closomer. The excess 1-bromopentane was removed using a high vacuum while the suspension was warmed to 50−60 °C. The remaining red residue was chromatographed on neutral alumina or silica. A yellow fraction was eluted with 20% EtOAc/80% hexanes, and a pink/purple fraction was eluted with EtOAc. Further oxidation of the purple fraction was performed as described in the general procedure. The overall yield of **5** was 78%.

Method 2. The reaction was conducted at 150 °C and 700 psi for 7 h. The reaction was monitored using ^{11}B NMR. When the reaction was complete, the workup procedure described above was employed. The neutral closomer **5** was isolated in 75% yield.

Compound **5** was obtained as a dark yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.0 Hz, 36 H), 1.32 (m, 48 H), 1.55 (m, 24 H), 4.02 (t, J = 6.4 Hz, 24 H). ^{13}C NMR (125.5 MHz, $CDCl_3$): δ 14.0, 22.4, 28.3, 31.8, 70.1. ^{11}B NMR (160 MHz, MeCN): δ 41.3. HRMS (MALDI): *m*/*z* calcd for$C_{60}H_{132}O_{12}B_{12}$ (M^-), 1175.1146; found, 1175.1160.

Dodeca(allyloxy)-*hypercloso*-dodecaborane (6). Method 1. After addition of 6.40 mL (74.0 mmol) of allyl bromide, the reaction mixture was refluxed for 7 d. The general procedure was followed to obtain **6**. *If the reaction mixture becomes dark brown in color, the reaction should be repeated. The product should be stored at −20 °C or used immediately.* The overall yield of **6** was 55%.

Method 2. The reaction was conducted at 150 °C and 700 psi for 3 h using allyl chloride. The reaction was monitored using ^{11}B NMR. Following completion of the reaction, the general oxidation procedure described above was followed and the remaining residue was chromatographed on neutral alumina. A yellow fraction corresponding to **6** was eluted with 20% EtOAc/80% hexanes, and a pink/purple fraction was eluted with EtOAc. The overall yield of **6** was 60%.

Compound **6** is a dark yellow-orange viscous oil. ^{1}H NMR (500 MHz, C_6D_6): δ 4.94 (d, J = 4.2 Hz, 24 H), 5.05 (dd, J = 10.2, 1.80 Hz 12 H), 5.37 (dd, J = 17.1,1.80 Hz, 12 H), 6.00 (m, 12 H). ^{13}C NMR (125.5 MHz, $CDCl_3$): δ 71.5, 114.2, 136.9. ^{11}B NMR (160 MHz, MeCN): δ 41.0. HRMS (MALDI): *m*/*z* calcd for $C_{36}H_{60}O_{12}B_{12}$ (M^-), 814.5298; found, 814.5304.

Dodeca(4-butenoxy)-*hypercloso*-dodecaborane (7). Method 1. The reaction mixture was refluxed for 19 d after addition of 7.40 mL (73.0 mmol) of 4-bromo-1-butene. The excess 4-bromo-1-butene was removed under high vacuum with warming at 50 °C. Following completion of the reaction, the general oxidation procedure described above was followed and the remaining residue was chromatographed on neutral alumina. A yellow fraction corresponding to **7** was eluted with 20% EtOAc/80% hexanes, and a pink/purple fraction was eluted with EtOAc.The overall yield of the closomer **7** was 65%. *Compound **7** should be stored at −20 °C or used immediately.*

Method 2. The reaction was conducted at 150 °C and 600 psi for 6 h. When the reaction was complete, the procedure described above for method 1 was employed. The neutral closomer **7** was isolated in 62% yield.

Compound **7** is a dark yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (dt, J = 6.30, 4.06 Hz, 24 H), 4.09 (t, J = 6.3 Hz 24 H), 4.93−5.02 (m, 24 H), 5.83 (dd, J = 17.2, 1.60 Hz, 12 H), 5.81 (m, 12 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 36.6, 70.0, 115.8, 136.1. ^{11}B NMR (160 MHz, MeCN): δ 41.4. HRMS (MALDI): *m*/*z* calcd for $C_{48}H_{84}O_{12}B_{12}$ (M^-), 982.7283; found, 982.7264.

Dodeca(3-methylbutoxy)-*hypercloso*-dodecaborane (8). Method 2. After addition of 7.55 mL (72.0 mmol) of 1-bromo-3-methylbutane, the reaction mixture was transferred by syringe into a 100 mL autoclave vessel equipped with a glass liner. The alkylation reaction was carried out at 150 °C and 1000 psi for 8 h. A yellow fraction was eluted with benzene, and a red/pink fraction was eluted with EtOAc using silica. Further oxidation of the red/pink fraction was performed as described in the general procedure. The closomer **8** was afforded in 75% yield.

Compound **8** is a dark-orange solid (sublimes at 185 °C, 1 atm). ^{1}H NMR (400 MHz, C_6D_6): δ 1.11 (d, J = 6.67 Hz, 72 H), 1.81 (q, J = 6.67, 13.4 Hz, 24 H), 2.05 (m, 12 H), 4.57 (t, J = 6.64 Hz, 24 H). ^{13}C NMR (125.5 MHz, C_6D_6): δ 22.7, 25.1, 41.6, 69.1. ^{11}B NMR (160 MHz, MeCN): δ 42.5. HRMS (MALDI): *m*/*z* calcd for $C_{60}H_{132}O_{12}B_{12}$ (M^-), 1175.0946; found, 1175.0913.

Dodeca(4-fluorobenzyloxy)-*hypercloso*-dodecaborane (9). Method 1. *This reaction should be carried out in the absence of light.* After addition of 9.00 mL (73.0 mmol) of 4-fluorobenzyl bromide, the reaction mixture was refluxed for 5 d under argon. *If the color of the reaction becomes yellow/brown, it should be discarded and the system should be checked for traces of oxygen and/or light.* The excess 4-fluorobenzyl bromide was removed using chromatography (neutral alumina) by employing 20% EtOAc/80% hexanes, and the pink/purple product mixture was eluted with EtOAc. The purple residue was oxidized according to the general procedures and then chromatographed on silica by employing 20% EtOAc/80% hexanes to elute a yellow fraction (**9**), and the remaining purple fraction was eluted with EtOAc. The overall yield of the closomer was 59%. *This compound should be stored at −20 °C or used immediately.*

Method 2. The reaction was carried out at 150 °C and 550 psi for 1 h using 4-fluorobenzyl chloride. When the reaction was complete, the purification procedure described in method 1, above, was followed. The neutral closomer **9** was isolated in 68% yield.

Compound **9** is an orange solid (melting point 162−164 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (s, 24 H), 6.88 (m, 24 H), 7.01 (m, 24 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 72.5, 115.1 (d, J_{C-F} = 21.6 Hz), 128.6 (d, J_{C-F} = 8.1 Hz), 135.7, 162.1 (d, J_{C-F} = 246.2 Hz). ^{11}B NMR (160 MHz, MeCN): δ 41.7. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −115.0. LRMS (MALDI): *m*/*z* calcd for $C_{84}H_{72}B_{12}O_{12}F_{12}$ (M^-), 1631.65; found, 1631.67.

Dodeca(3-fluorobenzyloxy)-*hypercloso*-dodecaborane (11). Method 2. *This reaction should be carried out in the absence of light.* Following the addition of 3.50 mL (30.0 mmol) of 3-fluorobenzyl chloride, the reaction was carried out at 150 °C and 1500 psi for 4 h. The excess 3-fluorobenzyl chloride was removed using chromatography on silica by employing benzene, and the purple product mixture was eluted with acetonitrile.

A 0.50 g sample of the purple residue was dissolved in 15.0 mL of 95% ethanol, 1.00 g of $FeCl_3 \cdot 6H_2O$ was added, and the resulting solution was stirred for 12 h at room temperature. Solvent was removed using a rotary evaporator. The remaining brown residue was dissolved in dichloromethane and chromatographed on silica. A yellow fraction (**11**) was eluted with dichloromethane, and the remaining pink/purple fraction was eluted with EtOAc. The overall yield of the neutral closomer was 60%.

Compound **11** is an orange solid (melting point 82.5−84.0 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.20 (s, 24 H), 6.79−6.94 (m, 36 H), 7.14−7.18 (m, 12 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 72.5, 113.4 (d, J_{C-F} = 21.8 Hz), 114.3 (d, J_{C-F} = 20.9 Hz), 122.0, 129.8 (d, J_{C-F} =8.0 Hz), 141.5 (d, J_{C-F} = 6.5 Hz), 162.1 (d, J_{C-F} = 244.9 Hz). ^{11}B NMR (160 MHz, CH_2Cl_2): δ 42.0. MS (MALDI): *m*/*z* calcd for $C_{84}H_{72}O_{12}B_{12}F_{12}$ (M^-), 1631.65; found, 1631.72.

Dodeca(4-chlorobenzyloxy)-*hypercloso*-dodecaborane (12). Method 2. *This reaction should be carried out in the absence of light.* After the addition of 5.90 g (36.0 mmol) of 4-chlorobenzyl chloride, the reaction was carried out at 150 °C and 1500 psi for 5 h. The excess 4-chlorobenzyl chloride was removed using chromatography on silica by employing benzene, and the purple product mixture was eluted with acetonitrile.

A 0.50 g sample of the purple residue was dissolved in 15.0 mL of 95% ethanol, 1.00 g of $FeCl_3 \cdot 6H_2O$ was added, and the resulting solution was stirred for 12 h at room temperature. Purification of **12** was accomplished by following the procedure described above for **11** to give a 75% yield.

Compound **12** is an orange solid (melting point 158.5−160.0 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.10 (s, 24H), 6.93 (d, J = 7.72 Hz, 24H), 7.17 (d, J = 7.88 Hz, 24H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 72.4, 128.0, 128.5, 133.4, 137.9. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 42.8. MS (MALDI): *m*/*z* calcd for $C_{84}H_{72}O_{12}B_{12}Cl_{12}$ (M^-), 1828.91; found, 1828.94

Dodeca(4-bromobenzyloxy)-*hypercloso*-dodecaborane (13). Method 2. *This reaction should be carried out in the absence of light.* After the addition of 4.60 g (18.3 mmol) of 4-bromobenzyl bromide, the reaction was carried out at 150 °C and 1500 psi for 5 h. The neutral form of **13** was obtained by following the procedure described for **11**. The overall yield of **13** was 70%.

Compound **13** is an orange solid (melting point 165.0−165.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.11 (s, 24 H), 6.89 (d, J = 8.23 Hz, 24 H), 7.37 (d, J = 6.72 Hz, 24 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 72.4, 121.5, 128.3, 131.4, 138.4. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 42.2. MS (MALDI): *m*/*z* calcd for $C_{84}H_{72}O_{12}B_{12}Br_{12}$ (M^-), 2360.99; found, 2360.98

Dodeca(3-bromobenzyloxy)-*hypercloso*-dodecaborane (14). Method 2. *This reaction should be carried out in the absence of light.* After 3.50 g (14.3 mmol) of 3-bromobenzyl bromide was added to the reaction mixture, the reaction was carried out at 150 °C and 1500 psi for 5 h. Purification and oxidation of **14** was carried out as described for **11.** The closomer was afforded in 65% yield.

Compound **14** is an orange solid (melting point 111.0−112.0 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.20 (s, 24 H), 7.02−7.13 (m, 24 H), 7.33−7.39 (m, 24 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 72.4, 122.5, 125.0, 129.5, 130.0, 130.6, 141.6. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 42.3. MS (MALDI): *m*/*z* calcd for $C_{84}H_{72}O_{12}B_{12}Br_{12}$ (M^-), 2360.99; found, 2360.94.

Dodeca(4-methylbenzyloxy)-*hypercloso*-dodecaborane (15). Method 2. After the addition of 3.50 mL (25.5 mmol) of 4-methylbenzyl chloride, the reaction was carried out at 150 °C and 1500 psi for 5 h. The acetonitrile and unreacted base were removed using a rotary evaporator. The yellow fraction was eluted with hexanes on silica. The excess 4-methylbenzyl chloride was removed by employing benzene, the purple product mixture was eluted with acetonitrile, and the solvent was removed by employing a rotary evaporator. The oxidation of the purple fraction was carried out as described for **11** to give a 55% yield.

Compound **15** is an orange/brown viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 36 H), 5.20 (s, 24 H), 6.96−6.99 (m, 48 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.0, 72.7, 127.1, 128.5, 136.2, 137.7. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 43.0. MS (MALDI) *m*/*z* calcd for $C_{96}H_{108}O_{12}B_{12}$ (M^-), 1584.02; found, 1584.08.

Dodeca(4-methoxybenzyloxy)-*hypercloso*-dodecaborane (16). Method 2. *If the color of the reaction becomes yellow/brown, the reaction should be repeated.* Following the addition of 3.50 mL (25.8 mmol) of 4-methoxybenzyl chloride, the reaction was carried out at 150 °C and 1500 psi for 1 h. The acetonitrile and unreacted base were removed using a rotary evaporator. The excess 4-methoxybenzyl chloride was removed by employing hexanes on silica. The yellow fraction was eluted with 30% diethyl ether/70% chloroform, the purple product mixture was eluted with acetonitrile, and the solvent was removed by employing a rotary evaporator.

The purple residue (0.5 g) was dissolved in 15.0 mL of 95% ethanol, 1.00 g of $FeCl_3 \cdot 6H_2O$ was added, and the resulting solution was stirred for 1 h at room temperature. Solvent was removed using a rotary evaporator. The remaining brown residue was dissolved in dichloromethane and chromatographed on silica. A yellow fraction (**16**) was eluted with 30% diethyl ether/70% chloroform, and the remaining pink/purple fraction was eluted with EtOAc. The overall yield of the closomer was 30%.

Compound **16** is an orange/brown viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (s, 36 H), 4.38 (s, 24 H), 6.80 (d, J = 8.40 Hz, 24 H), 7.19 (d, J = 8.40 Hz, 24 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 55.3, 71.5, 113.8, 129.4, 130.5, 159.2. ^{11}B NMR (160 MHz, CH_2Cl_2): δ 42.7. MS (MALDI): *m*/*z* calcd for $C_{96}H_{108}O_{24}B_{12}$ (M^-), 1775.19; found, 1775.2.

Alkylation of $(TBA)_2$-1 Using *p*-Toluenesulfonic Acid Esters: Dodeca(*n*-hexoxy)-*hypercloso*-dodecaborane (4). Method 2. In a 100 mL oven-dried Schlenk flask, 0.250 g (0.31 mmol) of $(TBA)_2$-**1** was dissolved in 15.0 mL of acetonitrile. Using a syringe, 1.00 mL (5.75 mmol) of *N*,*N*-diisopropylethylamine and 5.00 mL (22.0 mmol) of *n*-hexyl tosylate were added. Under argon the reaction mixture was placed into a 100 mL glass-lined autoclave vessel using a syringe. The reaction was conducted at 150 °C and 1100 psi for 2 h. The reaction mixture changed from yellow to purple during the reaction. Acetonitrile and unreacted base were removed using a rotary evaporator. The excess *n*-hexyl tosylate was removed using a high vacuum with warming at 70 °C. The oxidation and purification procedures were as described above to give **4** in a 70% yield.

Dodecamethoxy-*hypercloso*-dodecaborane (10). Method 2. In a 100 mL oven-dried Schlenk flask, 0.250 g (0.31 mmol) of $(TBA)_2$-**1** was dissolved in 15.0 mL of acetonitrile. Using a syringe, 1.00 mL (5.75 mmol) of *N*,*N*-diisopropylethylamine and 5.00 mL (37.0 mmol) of methyl tosylate were added. Under argon, the reaction mixture was placed into a 100 mL glass-lined autoclave vessel via syringe. The reaction was run at 150 °C and 1300 psi for 2 h. The reaction mixture passed through a series of different colors starting with yellow, then light pink, and finally purple. The acetonitrile and unreacted base were removed using a rotary evaporator. The excess methyl tosylate was removed utilizing a high vacuum with warming at 80 °C. The purification and oxidation procedures employed for **3** were followed to give **10** in a 50% yield.

Compound **10** is a dark-orange solid (sublimes at 130 °C, 1 atm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 36 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 58.9. ^{11}B NMR (160 MHz, MeCN): δ 37.5. HRMS

(MALDI): *m*/*z* calcd for $C_{12}H_{36}O_{12}B_{12}$ (M^-), 502.3407; found, 502.3418.

Crystallographic Studies. All measurements were made on a Bruker Smart 1000 diffractometer equipped with a Mo tube. Data for **2** and **3** were collected at 100 K, while data for the other compounds were collected at 25 °C. Calculations were made using software furnished by Bruker. The conditions of the data collection have been tabulated, and atoms were located by direct methods. None of these molecules crystallize with solvent.

Dodecaethoxy-*hypercloso*-dodecaborane (3). A deep red parallelepiped obtained from a CH_3OH solution was mounted on a thin glass fiber. Data were corrected for absorption. There are two crystallographically different types of molecules in the unit cell. In molecule A the unique part is 1/6, and this molecule has a 3-fold axis and is also centrosymmetric. The other two molecules in the unit cell each have a 3-fold axis, and they are related to each other by a center of symmetry. The unique part of molecule B is 1/3.

Dodeca(4-fluorobenzyloxy)-*hypercloso*-dodecaborane (9). A deep red crystalline cut needle obtained from a toluene solution was mounted on a thin glass fiber. No absorption correction was applied to these data. The molecule is centrosymmetric and has a 3-fold axis (the unique part is 1/6).

Dodeca(3-fluorobenzyloxy)-*hypercloso*-dodecaborane (11). A red crystalline parallelepiped obtained from a toluene solution was mounted on a thin glass fiber. Data were corrected for extinction, but not for absorption. The molecule is centrosymmetric, and the unique part of the molecule is 1/2.

Dodeca(4-chlorobenzyloxy)-*hypercloso*-dodecaborane (12). A deep red crystalline needle obtained from a benzene solution was mounted on a thin glass fiber. Data were not corrected for absorption. The molecule is centrosymmetric, and the unique part is 1/2.

Dodeca(4-bromobenzyloxy)-*hypercloso*-dodecaborane (13) and Dodeca(3-bromobenzyloxy)-*hypercloso*-dodecaborane (14). A deep red crystalline plate obtained from a toluene solution was mounted on a thin glass fiber. Data were corrected for absorption. The molecule is centrosymmetric, and the unique part is 1/2.

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Supporting Information Available: Experimental procedures and ^1H, ^{13}C, and ^{11}B NMR and mass spectra of all compounds (PDF) and CIF files for compounds **3**, **9**, **11**, **12**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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