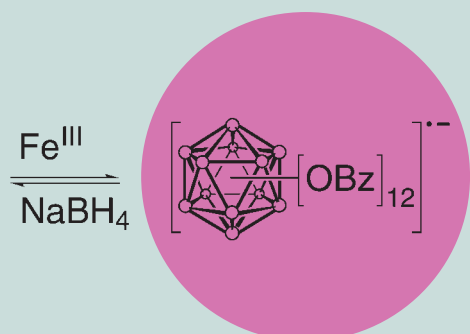
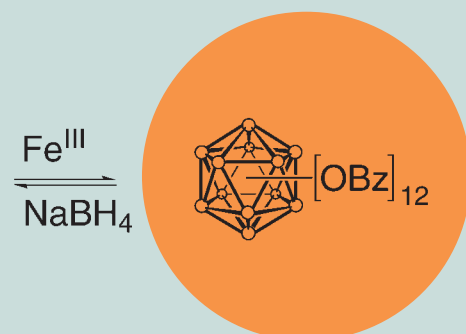


closo



hypercloso



hypercloso



Globular molecules with an icosahedral core—12(12)-closomers—are obtained by total esterification of $[\text{B}_{12}(\text{OH})_{12}]^{2-}$.

For details as well as for the transformation of an anionic ester into the neutral *hypercloso* analogue see the following two communications.

Twelfold Functionalization of an Icosahedral Surface by Total Esterification of $[\text{B}_{12}(\text{OH})_{12}]^{2-}$: 12(12)-Closomers**

Andreas Maderna, Carolyn B. Knobler, and M. Frederick Hawthorne*

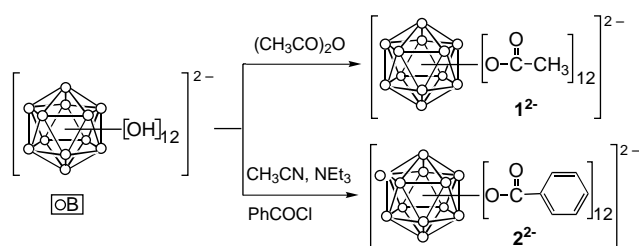
The synthesis of globular molecules in which precisely constructed organic chains are grown from the vertices of closed polyhedra (defined here as closomers^[1]) has remained a challenge to chemists interested in new applications ranging from materials science to medicine. Intense interest in the related chemistry of dendrimers, macromolecules having regular and highly branched architectures,^[2] suggested the challenge of closomer synthesis. Closomers may retain the globular nature of dendrimers while introducing as variables the discrete properties of the polyhedral core (e.g. geometry, number of reactive vertices, electronic structure, ionic charge, redox capabilities, paramagnetism, chromophoric properties, and hydrophobicity).

Only a few polyhedral clusters have been evaluated for this purpose, the most prominent being C_{60} . Hirsch et al. synthesized C_{60} derivatives containing up to six amphiphilic dendritic substituents and used these compounds to form artificial membranes and vesicles.^[3, 4] Other cluster species bearing multiple organic substituents include silsesquioxanes, siloxane clusters in which each silicon atom is bridged by three oxygen atoms and attached to an organic moiety.^[5]

Of special interest for use as closomer cores are the polyhedral boranes and carboranes. The parent aromatic polyhedral borane $[\text{closo-B}_{12}\text{H}_{12}]^{2-}$ is a robust icosahedral cluster stabilized by three-dimensional delocalization of thirteen bonding electron pairs.^[6, 7] We recently reported the efficient perhydroxylation of $[\text{closo-B}_{12}\text{H}_{12}]^{2-}$ by treatment with 30% hydrogen peroxide leading to $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$.^[8]

Here we report the synthesis of closomers derived from $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ in which each hydroxy function is converted into a carboxylate ester. The syntheses of closomers containing benzyl ether substituents and having the B_{12} core charges -2 , -1 , and 0 are reported in the subsequent communication.^[9]

The dodecaacetate $\mathbf{1}^{2-}$ (Scheme 1) was formed in 43% yield by reaction of $\text{Cs}_2[\text{closo-B}_{12}(\text{OH})_{12}]$ with acetic anhydride at the reflux temperature for three days. $\text{Cs}_2\text{-1}$ is soluble in water and methanol and moderately soluble in acetonitrile and acetone. The ^{11}B NMR spectrum of $\text{Cs}_2\text{-1}$ shows a symmetrical singlet at $\delta = -16$ which is not significantly different from that of the starting material, $\text{Cs}_2[\text{closo-B}_{12}(\text{OH})_{12}]$. However, if the esterification reaction does not proceed to completion the



Scheme 1. Esterification of $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ with acetic anhydride or benzoyl chloride leads to a total organoderivatization of its icosahedral surface: syntheses of the 12(12)-closomers^[1] $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$.

^{11}B NMR spectrum of the partly esterified $[\text{closo-B}_{12}(\text{OH})_{12-n}(\text{OAc})_n]^{2-}$ ($n = 1-11$) appears as an asymmetric signal resulting from the reduced symmetry of the B_{12} icosahedron. In this case, the reaction with acetic anhydride can be repeated to complete the esterification of all twelve hydroxy functions. The ^1H NMR spectrum of $\text{Cs}_2\text{-1}$ exhibits a singlet at $\delta = 1.9$ for the methyl protons; the ^{13}C NMR spectrum displays a signal at $\delta = 174$ for the carbonyl functions and a signal at $\delta = 22$ for the methyl groups. The electrospray mass spectrum (negative mode) reveals the molecular ion peak of $\mathbf{1}^{2-}$ at m/z 839.2, $[\mathbf{1}^{2-} + \text{H}]^-$, and a peak for the dinegatively charged cluster at m/z 419.1, $\mathbf{1}^{2-}$. Figure 1 presents the result of the single-crystal X-ray structure analysis of $\text{Cs}_2\text{-1}$.^[10] Dianion $\mathbf{1}^{2-}$ is centrosymmetric and the B_{12} cage has approximate icosahedral symmetry with B–B bond lengths ranging from 1.776(3) to 1.843(3) Å and B–O bond lengths of 1.440(2) to 1.449(2) Å.

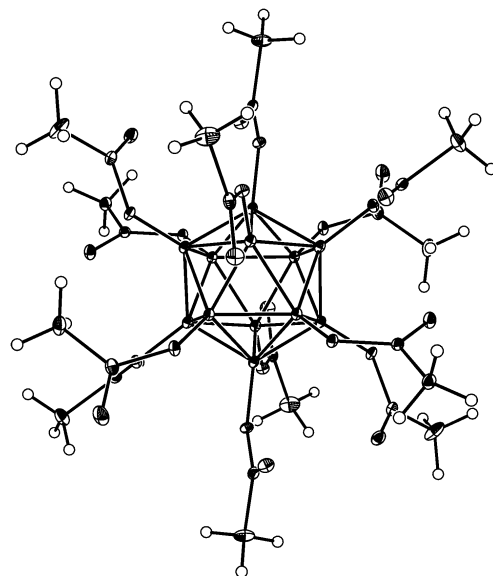


Figure 1. Structure of the dodecaacetate ester $\mathbf{1}^{2-}$ (ORTEP diagram). The ellipsoids represent a 30% probability level.

An important requirement for the success of the closomer esterification reaction is the dissolution of the $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ ion reactant, whose solubility is dependent upon the identity of the cations employed. The dicesium salt, $\text{Cs}_2[\text{closo-B}_{12}(\text{OH})_{12}]$, is only soluble in warm water and is partially soluble in carboxylic acid anhydrides containing short carbon chains, such as acetic or propionic anhydrides, and at elevated temperatures. Conversion of the Cs_2 salt into

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the $[\text{Bu}_4\text{N}]_2$ salt increases the solubility of $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ in organic solvents and enables the synthesis of carboxylate esters from acid chlorides in 1,2-dichloroethane or acetonitrile at their reflux temperatures. Reaction of $[\text{NBu}_4]_2[\text{closo-B}_{12}(\text{OH})_{12}]$ with an excess of benzoyl chloride in the presence of triethylamine in acetonitrile gave the dodecabenzoate ester $\mathbf{2}^{2-}$ in 52% yield following a reaction time of 10 days (Scheme 1). The electrospray mass spectrum of $\mathbf{2}^{2-}$ in the negative mode reveals a peak at m/z 1584.0 for $[\mathbf{2}^{2-}+\text{H}]^-$ and a peak at m/z 791.5 for $\mathbf{2}^{2-}$. Surprisingly, the electrospray mass spectrum in the positive mode does not indicate the presence of equivalent amounts of the cations expected for $\mathbf{2}^{2-}$. The data reveal a significant disparity in the signal strengths of the observed negative ions and the observed positive ions of the same sample.^[11] The ^1H and ^{13}C NMR data display the signals expected for $\mathbf{2}^{2-}$ alone, while the ^{11}B NMR spectrum shows a symmetrical singlet at $\delta = -16$. Based on the mass spectrometry and NMR data, which both lack the presence of a detectable cation in amounts equivalent to $\mathbf{2}^{2-}$, we surmise that the dodecabenzoate $\mathbf{2}^{2-}$ was isolated in its diprotonated form $[\text{H}]_2\mathbf{2}$ or as a dihydronium salt $[\text{H}_3\text{O}]_2\mathbf{2}$. This assumption is supported by the existence of a weak signal in the electrospray mass spectrum in the positive mode at m/z 1586 for $[\mathbf{2}^{2-}+3\text{H}]^+$. The existence of this positive closomer ion indicates that the multiple protonation of $\mathbf{2}^{2-}$ is indeed possible. At present we cannot determine whether $\mathbf{2}$ was isolated as $[\text{H}]_2\mathbf{2}$ or $[\text{H}_3\text{O}]_2\mathbf{2}$, but to simplify the further discussion we will assume it to be the dihydronium salt $[\text{H}_3\text{O}]_2\mathbf{2}$. This species was presumably formed during the chromatographic purification of $\mathbf{2}^{2-}$ on silica gel by interaction of $\mathbf{2}^{2-}$ with proton sources associated with the silica. The species assumed to be $[\text{H}_3\text{O}]_2\mathbf{2}$ is soluble in dimethyl sulfoxide and dimethylformamide and poorly soluble in acetonitrile and methanol.

Addition of tetraphenylarsonium chloride to a solution of $[\text{H}_3\text{O}]_2\mathbf{2}$ in dimethylformamide gave $[\text{Ph}_4\text{As}]_2\mathbf{2}$ as a white solid which is quite soluble in methanol and acetonitrile. Figure 2 displays the result of an X-ray structure analysis of

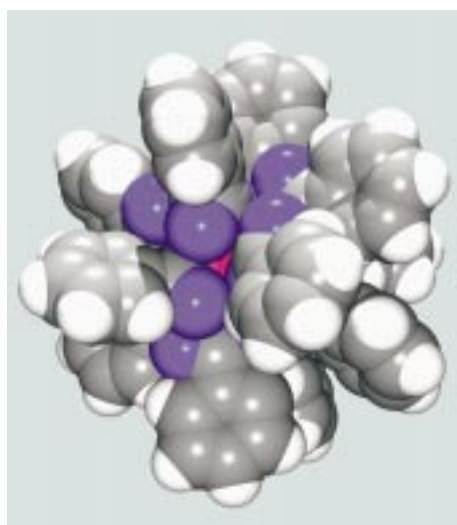
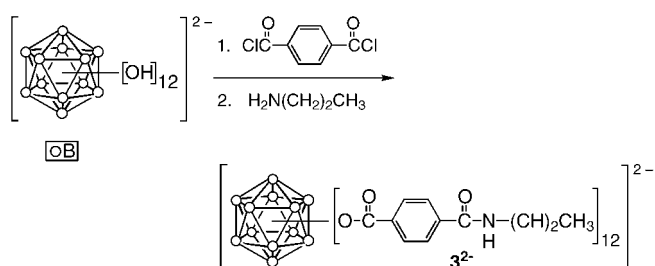


Figure 2. Space-filling representation of the structure of the dodecabenzoate ester $\mathbf{2}^{2-}$. White H; gray C; purple O; magenta B. The B_{12} cluster is almost completely camouflaged by the twelve benzoyloxy groups.

$[\text{Ph}_4\text{As}]_2\mathbf{2}$ as a space-filling representation.^[10b, 12] The ion $\mathbf{2}^{2-}$ is centrosymmetric with approximate icosahedral symmetry in the B_{12} cage; the B–B distances range from 1.768(4) to 1.828(4) Å, and the B–O distances from 1.416(3) to 1.429(3) Å. The space-filling representation of $\mathbf{2}^{2-}$ displays the impressive camouflage of the dinegatively charged B_{12} cluster by the twelve benzoyloxy groups which almost completely cover its icosahedral surface.

Of particular interest for the use of closomers as cores for the further synthesis of macromolecules and dendritic structures is the development of a synthetic strategy which provides additional connecting sites for chain functionalization and extension. One way of approaching this goal is the utilization of bifunctional carboxylic acid chlorides which link each hydroxy group in $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ with a primary or secondary amine. This strategy was successfully demonstrated by the reaction of $[\text{NBu}_4]_2[\text{closo-B}_{12}(\text{OH})_{12}]$ with excess terephthaloyl chloride followed by addition of *n*-propylamine (Scheme 2). The formation of the *n*-propylamine-linked



Scheme 2. Functionalization of 12(12)-closomers^[1] with twelve amide groups by employing terephthaloyl chloride for the esterification of $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ followed by reaction with *n*-propylamine.

closomer $\mathbf{3}^{2-}$ was proved by fast atom bombardment (FAB) mass spectrometry which revealed its molecular ion peak at m/z 2604 for $[\mathbf{3}^{2-}+\text{H}]^-$. An optimized procedure for $\mathbf{3}^{2-}$ and conceptually related species is currently being developed in our laboratories and will be reported elsewhere.

The synthesis of esters employing acid anhydrides or acid chlorides is one of the oldest known organic reactions. The simplicity of this chemistry contrasts with the novelty of the 12(12)-closomer^[1] esters described here in that *all* hydroxy groups in $[\text{closo-B}_{12}(\text{OH})_{12}]^{2-}$ can be converted into ester functions leading to total organoderivatization of its icosahedral surface. The resulting 12(12)-closomers represent the first examples of this structural motif known in chemistry. These new closomeric structures can provide camouflaged mono-dispersed molecules and nanoparticles of variable size, shape, charge, hydrophobicity, etc., designed to accomplish a huge variety of specific functions important to a broad spectrum of technology ranging from materials science to biomedicine.

Experimental Section

Solvents and liquid reagents were dried and distilled according to standard procedures.

All reactions were carried out under moisture-free conditions using argon as the inert gas. $[\text{NBu}_4]_2[\text{closo-B}_{12}(\text{OH})_{12}]$ was obtained from $\text{Cs}_2[\text{closo-}$

$B_{12}(OH)_{12}$]^[8] by cation exchange using cation exchange resin and was dried at 60 °C in vacuo for 24 h before use. NMR spectra were obtained on a Bruker ARX 500 spectrometer, electrospray mass spectra on a Perkin-Elmer Sciex API III triple quadrupole mass spectrometer, and FAB mass spectra were obtained on a VG ZAB-SE mass spectrometer.

Cs₂-1: A suspension of Cs₂[*closo*-B₁₂(OH)₁₂] (48 mg, 0.080 mmol) in acetic acid anhydride (6 mL) was heated with stirring at reflux for three days under argon. The brown reaction mixture was cooled to room temperature and the volatiles were removed in vacuo. The residue was dried in vacuo at 50 °C for 10 h. The solid was dissolved in water (6 mL) at room temperature, the suspension filtered, and the filtrate cooled at 3 °C for 60 min. The resulting suspension was again filtered using a 0.2 μm filter and the water removed in vacuo to give Cs₂-1 as a light brown solid in sufficient purity for further use (38 mg, 0.034 mmol, 43%). Further purification can be achieved by recrystallization from acetic anhydride. Single crystals suitable for X-ray structure analysis were obtained from a solution in acetonitrile/water with the addition of a small amount of thiourea. ¹H NMR (500 MHz, D₂O): δ = 1.9 (s); ¹³C NMR (126 MHz, D₂O): δ = 22.0 (Me), 174.0 (CO); ¹¹B NMR (160 MHz, D₂O): δ = -16; ESI-MS (negative mode, water): *m/z*: 839.2 [$1^{2-} + H$]⁻, 419.1 1^{2-} .

[H₃O]₂-2: To a suspension of [NBu₄]₂[*closo*-B₁₂(OH)₁₂] (47 mg, 0.058 mmol) in dry acetonitrile (30 mL) were added benzoyl chloride (0.40 mL, 480 mg, 3.5 mmol) and dry triethylamine (2 mL, 1.452 g, 14.3 mmol). The reaction mixture was heated with stirring at reflux for 10 days under argon. The brown suspension was cooled to room temperature, filtered, and the volatiles were removed in vacuo. The resulting dark brown solid was purified by filtration over silica gel by employing CH₂Cl₂, followed by THF, and finally acetonitrile as the mobile phases. The first two mobile phases eluted colored impurities and elution was continued until the eluate was colorless. The mobile phase was then changed to acetonitrile. The acetonitrile fractions were collected, the solvent was removed in vacuo, and the solid was washed with THF and warm water to give pure [H₃O]₂-2 as a white solid (49 mg, 0.030 mmol, 52%). ¹H NMR (500 MHz, [D₆]DMSO): δ = 8.0 (m, 24H), 7.4 (m, 12H), 7.1 (m, 24H); ¹³C NMR (126 MHz, [D₆]DMSO): δ = 163.6 (CO), 134.7, 130.7, 130.1, 127.2; ¹¹B NMR (160 MHz, [D₆]DMSO): δ = -16; ESI-MS (negative mode, acetonitrile): *m/z*: 1584.0 [$2^{2-} + H$]⁻, 791.5 2^{2-} .

[Ph₄As]₂-2: To a solution of [H₃O]₂-2 (40 mg, 0.025 mmol) in DMF (2 mL) was added a solution of [Ph₄As]Cl (31 mg, 0.074 mmol) in DMF (2 mL). Subsequent addition of water (4 mL) gave [Ph₄As]₂-2 as a white precipitate which was washed twice with warm water and dried in vacuo (59 mg, 0.025 mmol, 100%). Single crystals suitable for X-ray structure analysis were obtained from a solution in methanol.

¹H NMR (500 MHz, CD₃CN): δ = 8.0 (m, 24H), 7.8 (m, 8H), 7.7 (m, 16H), 7.6 (m, 16H), 7.4 (m, 12H), 7.1 (m, 24H); ¹³C NMR (126 MHz, CD₃CN): δ = 165.1 (CO), 135.7, 135.4, 134.1, 131.8, 131.7, 131.0, 128.3; ¹¹B NMR (160 MHz, CD₃CN): δ = -15.

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- [1] Closomers are defined as polyhedra whose surfaces support polyatomic substituents. In the formulation below, the first number indicates the total number of cluster vertices potentially available for substitution, while the second number refers to the number of attached substituents. The designation 12(12)-closomer indicates a polyhedron containing 12 vertices and 12 substituents.
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- [10] a) Cs₂-1 · 2SC(NH₂)₂, triclinic, space group $P\bar{1}$ with *a* = 10.953(6), *b* = 11.334(7), *c* = 11.532(7) Å, α = 91.918(11)°, β = 113.221(9)°, γ = 112.575(9)°, *V* = 1185.6(12) Å³, *Z* = 1. Data were collected on a Bruker SMART 1000 using MoK_α radiation, 2θ_{max} = 56°, giving 5436 unique reflections and the structure was solved by direct methods. The final discrepancy index was *R* = 0.020, *R_w* = 0.048 for 4914 independent reflections with *I* > 2σ(*I*). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151203 (Cs₂-1 · 2SC(NH₂)₂) and CCDC-151204 ([Ph₄As]₂-2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [11] The signal strengths in the negative ion mode for 2^{2-} and [$2^{2-} + H$]⁻ relative to the cations observed in the positive ion mode was estimated from the ratio of signal intensities obtained in the two modes under identical scanning and detector settings with the same solution and in the absence of reagents that might enhance ion intensities in either mode and assuming similar ionization efficacy for positive and negative ions. For a salt with the composition AB₂ (A: anion, B: cation) the signal intensities for the negative and the positive ions are expected to be equivalent to the ratio of 1:2. The measured signal intensities of anions and cations in the same sample reveal only a ratio of about 1:0.18.
- [12] [Ph₄As]₂-2, triclinic space group $P\bar{1}$ with *a* = 13.873(2), *b* = 15.680(2), *c* = 16.280(2) Å, α = 65.368(2)°, β = 66.727(2)°, γ = 80.638(2)°, *V* = 2957.2(7) Å³, *Z* = 1. Data were collected on a Bruker SMART ccd diffractometer using MoK_α radiation, 2θ_{max} = 56.6°, giving 13554 unique reflections and the structure was solved by Patterson and heavy atom methods. The final discrepancy index was *R* = 0.054, *R_w* = 0.159 for 7763 independent reflections with *I* > 2σ(*I*).^[10b]

Dodeca(benzyloxy)dodecaborane, B₁₂(OCH₂Ph)₁₂: A Stable Derivative of hypercloso-B₁₂H₁₂**

Toralf Peymann, Carolyn B. Knobler, Saeed I. Khan, and M. Frederick Hawthorne*

In agreement with Wade's rules, the framework of a polyhedral borane requires 2*n*+2 (*n* = number of vertices) skeletal electrons to form a *closo* cage.^[1] These rules have been employed to successfully classify and rationalize the structures of the polyhedral boranes.^[2] Exceptions to Wade's rules have been reported for species having an apparent *closo* structure in which the number of framework electrons is less than the required 2*n*+2. These electron-deficient cages are

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