Icosahedral Building Blocks: Towards Dendrimers with Twelve Primary Branches?

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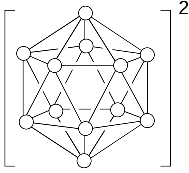
One of the early advances in the development of boron cluster chemistry was the structural characterization of $[B_{12}H_{12}]^{2-}$ by Lipscomb et al.,[1] and with it the confirmation of the icosahedral symmetry of the cage. In the last 40 years[2, 3] an astonishing wealth of boron-containing cluster derivatives including those based on carbaborane cores has been prepared, and these species have presented theorists with seemingly never-ending questions regarding bonding and electron bookkeeping. The icosahedral $[B_{12}H_{12}]^{2-}$ (**1**), 1,2-$C_2B_{10}H_{12}$ (**2**), and the 1,7- and 1,12-isomers of **2** remain some of the most studied clusters; their high stability has allowed an extensive chemistry to be developed.



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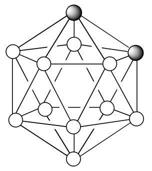

● = CH ○ = BH

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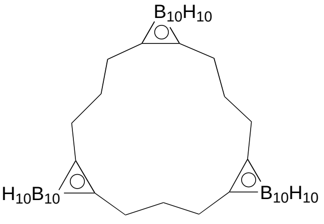
Nonetheless, the bulk of the documented compounds contain *single* cages. Multifunctionalization of borane and carbaborane clusters has been reported relatively rarely. Early contributions were chlorination and bromination reactions of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$.[4] The last few years have witnessed further progress with results, for example, from the groups of Hawthorne (permethylation of $C_2B_{10}H_{12}$ and $Me_2C_2B_{10}H_{10}$ and related species, and formation of 1,2-$C_2H_2B_{10}(CHCl_2)_{10}$),[5–7] Paetzold (perbrominated, periodinated, and permethylated derivatives of the azaboranes 4-$ClC_6H_4NB_9H_9$ and $MeNB_{11}H_{11}$),[8] Wilbur (periodination of 1,2- and 1,7-$C_2B_{10}H_{12}$ and monocarbon carboranes),[9] and Michl (preparation of $[CB_{11}Me_{12}]^-$ and the stable radical $CB_{11}Me^{\bullet}_{12}$, the first neutral metal-free, boron cluster radical to be isolated).[10, 11] Multifunctionalization of the cage is a significant step forward and should allow a breakthrough in the development of a new field of borane and carbaborane cluster chemistry, one which should take boron clusters firmly into the realm of the supramolecular explorer.

To date, functionalization at the C atoms of carbaborane cages has led to numerous derivatives, and of particular interest to the present perspective is the connection of clusters into cyclic arrays: for example arene-coupled systems,[12] a related cyclic trimer formed by treatment of 2,6-$Br_2H_3C_5N$ with 1,7-Cu_2-1,7-$C_2B_{10}H_{10}$ from Wade and co-workers,[13] and macrocycles such as **3** and **4** from the Hawthorne group.[14–16] Macrocycle **4** is of special interest because it acts as a host for a halide ion, and, thus, we approach the convergence of borane and supramolecular chemistries. Protection of the carbon sites of the C_2B_{10} cage has allowed access to an $Hg_3(cage)_3$ macrocycle with a framework which is supported by Hg–B links.[17] This step highlights an important synthetic strategy developed by Hawthorne et al.:[18] the production of mono- or bis-C-protected carbaborane clusters which will allow 1) controlled syntheses of monosubstituted clusters, or 2) complete protection of the carbon sites and synthesis of B-functionalized compounds. C-Protection by an alternative route has been developed by Teixidor, Viñas, and co-workers.[19]



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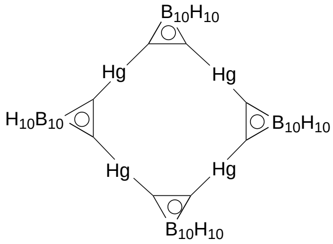

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△ $B_{10}H_{10}$ = 1,2-$C_2B_{10}H_{10}$

Within our own group, the coupling of cluster and supramolecular chemistries has been a recent goal; it has been the strategy of C-protection that has led to the successful preparation of, for example, 2,2′:6′,2″-terpyridine derivative **5** and the incorporation of $C_2B_{10}H_{10}$ cluster units on the surface of a number of dendrimers as in the first-generation dendrimer **6**. Here, the interactions that make the system "supramolecular" are the coordinate bonds: the octahedral coordination sphere of each Ru^{II} center directs the assembly which is initially centered on a tetrahedral carbon atom.[20]

Assembly through hydrogen bonding is exemplified by vast numbers of systems, of which two of the most cited are ice and DNA. Hydrogen bonding is essential to the stabilization of the crystalline frameworks of boric acid (**7**) and borate minerals. This point is made in the introduction to the watershed paper by Hawthorne et al.[21] in which the per-B-hydroxylated boron clusters $[B_{12}(OH)_{12}]^{2-}$ (**8**), $[1\text{-}H\text{-}1\text{-}CB_{11}(OH)_{11}]^-$, and 1,12-$H_2$-1,12-$C_2B_{10}(OH)_{10}$ are reported; structural data for **8** and 1,12-H_2-1,12-$C_2B_{10}(OH)_{10}$ show the retention of icosahedral cages.

The perhydroxylated derivatives[21] are made by treating alkali metal salts of $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^-$, as well as 1,12-$(CH_2OH)_2$-1,12-$C_2B_{10}H_{10}$ with 30% hydrogen peroxide at reflux temperature. The use of 1,12-$(CH_2OH)_2$-1,12-$C_2B_{10}H_{10}$ in place of 1,12-$C_2B_{10}H_{12}$ was required for the sake of

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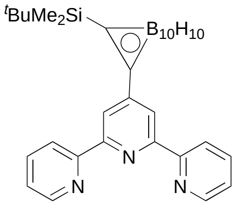

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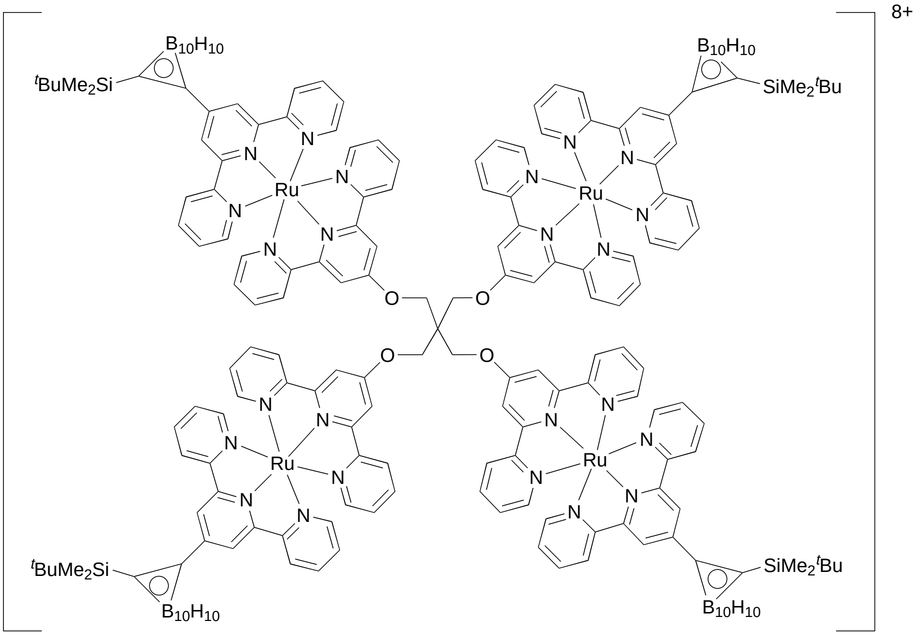

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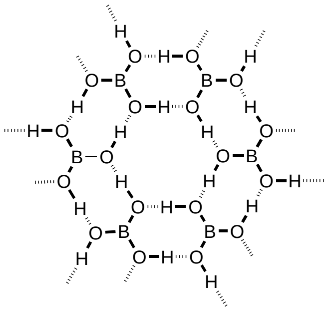

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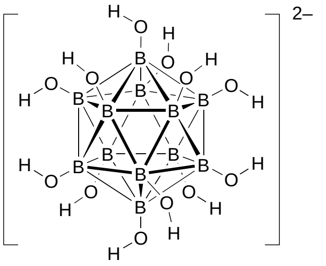

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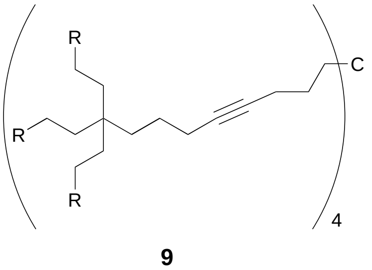
solubility in aqueous medium; the CH_2OH substituents are converted into H substituents during the course of the reaction. That a hydrogen-bonded, supramolecular network is formed is reflected, for example, in the insolubility of 1,12-H_2-1,12-$C_2B_{10}(OH)_{10}$ in water; it crystallizes as the dihydrate, and the hydrogen-bonded lattice involves the cage OH groups, the waters of crystallization, and the cage CH groups. Alkali metal salts of **8** show an interesting trend in solubilities: the Cs^+ salt can be crystallized from water, but the Li^+, Na^+, and K^+ salts precipitate when MCl (M = Li, Na, K) is added to aqueous solutions of the Cs^+ salt. This trend is attributed to the ability of **8** to function as a polyhapto ligand, entering and displacing the hydration spheres of the smaller M^+ ions and forming a hydrogen-bonded network that results in an insoluble salt.

The hydrogen-bonded arrays observed in the new clusters by Hawthorne and co-workers are, in themselves, fascinating. They point to the potential that $[B_{12}(OH)_{12}]^{2-}$ **8** has in the development of species which are a marriage of polyhedral borane and borate chemistries.[21] However, the isolation of icosahedral cages, the surfaces of which are covered in OH substituents, surely begs the question of using these cages as the central cores for the divergent growth of dendrimers.[22] The core is rigid and the directions of the "arms" within the first generation should be sterically favorable. In our own work, dendrimers such as **6** arise from polyhydroxylated cores, for example pentaerythritol.[20, 23] Our aim is to generate surface-functionalized dendrimers. A rather different approach has been taken by Newkome et al. in the reactions of dendritic skeletons, represented by **9**, with $B_{10}H_{14}$ to generate carbaborane-containing dendrimers.[24] In contrast to our strategy and that of Newkome et al., the perhydroxylated clusters described by Hawthorne et al.[21] offer a new direction to the field. Will a twelve-arm star molecule followed by dendritic derivatives be achievable targets?



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