

Carboranes

Carboranes are electron-delocalized (non-classically bonded) clusters composed of boron, carbon and hydrogen atoms that may also contain other metallic and nonmetallic elements in the cluster framework. Like many of the related boron hydrides, these clusters are polyhedra or fragments of polyhedra, and are similarly classified as *closo*-, *nido*-, *arachno*-, *hypho*-, etc., based on whether they represent a complete (*closo*-) polyhedron or a polyhedron that is missing one (*nido*-), two (*arachno*-), three (*hypho*-), or more vertices. Carboranes are a notable example of heteroboranes.

Carboranes have as few as 5 and as many as 14 atoms in the cage framework (15 if metal atoms are included) are known, but the majority have two cage carbon atoms; of these, the best-known series is that of the *closo*-C₂B_nH_{n+2} systems, where *n* = 3 to 12. However, carboranes having 1 to 6 cage carbon atoms have been prepared, as have a number of carborane mono- and dianions. The icosahedral CB₁₁H₁₂⁻ anion has a strong conjugate acid, whose polychlorinated derivative H(CHB₁₁Cl₁₁) is even a superacid.

The icosahedral charge-neutral *closo*-carboranes, 1,2-, 1,7-, and 1,12-C₂B₁₀H₁₂ (respectively *ortho*-, *meta*-, and *para*-carborane in the informal nomenclature) are particularly stable and are commercially available.^[3] These boron-rich clusters exhibit unique *organomimetic* properties with chemical reactivity matching classical organic molecules, yet are structurally similar to metal-based inorganic and organometallic species^[4]

The C₂B₁₀H₁₂ isomers, together with other carborane clusters and metallacarboranes (see below) are utilized in a wide range of applications, including heat-resistant polymers, recovery of radioactive metals from nuclear waste, catalysis, novel electroactive materials, and medical applications. Like for other electron-delocalized polyhedral clusters, the electronic structure of these cluster compounds can be described by the Wade–Mingos rules.^[5]

As noted above, carboranes are closely related to boron hydrides (boranes), and thus are structurally very different from hydrocarbons, owing to the fact that carbon atoms have one more valence electron than do boron atoms (a notable feature of carboranes is that the cage

carbon atoms often are directly bound to as many as 6, or even more, neighboring atoms, quite unlike the hydrocarbons).

Carboranes and boranes adopt 3-dimensional cage (cluster) geometries in order to facilitate their electron-delocalized nonclassical bonding, whereas hydrocarbons are typically chains or rings; for example, B₄H₁₀ has an *arachno* cage geometry, while the butane isomers *n*- and *iso*-C₄H₁₀, with 4 more electrons than B₄H₁₀, adopt linear or branched chain structures. Examples of *nido* and *arachno*- carboranes include 2,3-C₂B₄H₈ and 1,3-C₂B₇H₁₃ respectively. Geometrical isomers of carboranes can exist, necessitating the use of the numerical prefixes in a compound's name; this is illustrated by the 1,2-, 1,7-, and 1,2-C₂B₁₀H₁₂ icosahedral clusters referred to earlier.

Preparation

Carboranes have been prepared by many different routes, the most common being addition of alkynyl reagents to boron hydride clusters to form dicarbon carboranes. For example, the high-temperature reaction of pentaborane(9) with acetylene affords several *closo*-carboranes as well as other products:

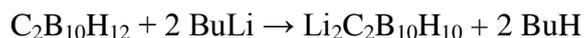


When the reaction is conducted at lower temperatures, an open-cage carborane is obtained:



Reactions

Carboranes undergo a wide variety of reactions. Deprotonation of *closo*-dicarbododecaboranes using organolithium reagents gives the dilithio derivatives.



These dilithiated compounds react with a variety of electrophiles, e.g. chlorophosphines, chlorosilanes, and sulfur.

Base-induced degradation of carboranes give anionic *nido* derivatives, which can be employed as ligands for transition metals, generating metallocarboranes, which are carboranes containing one or more transition metal or main group metal atoms in the cage

framework. Most famous is dicarbollide, with the formula $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$. These ligands form sandwich complexes.^[13] The bulk of the work on metallocarboranes has centered on 12-vertex MC_2B_9 and $\text{M}_2\text{C}_2\text{B}_8$ clusters and 7-vertex MC_2B_4 and $\text{M}_2\text{C}_2\text{B}_3$ (triple-decker and multidecker sandwich clusters, but metallocarboranes of 6 to 15 vertices have also been prepared, as have clusters with varying numbers of carbon, boron, and metal atoms. Diboroly-metal complexes featuring MC_3B_2 and $\text{M}_2\text{C}_3\text{B}_2$ cages, representing another type of metallocarborane, have also been extensively studied.