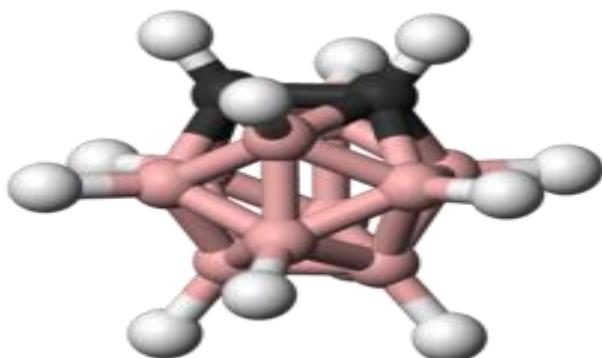


Carborane

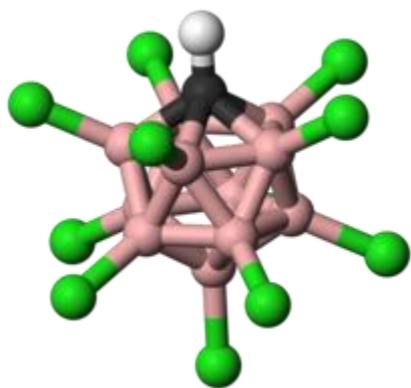
A **carborane** is a cluster composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedral and are similarly classified as *closo*-, *nido*-, *arachno*-, *hypho*-, etc. based on whether they represent a complete (*closo*-) polyhedron, or a polyhedron that is missing one (*nido*-), two (*arachno*-), or more vertices. Carboranes are notable example of heteroborane

Interesting examples of carboranes are the extremely stable icosahedra *closo*-carboranes. These boron-rich clusters exhibit unique organ mimetic properties with chemical reactivity matching classical organic molecules, yet structurally similar to metal-based inorganic and organ metallic species.

A prominent example is the charge-neutral $C_2B_{10}H_{12}$ or *o*-carborane with the prefix *o* derived from ortho, which has been explored for use in a wide range of applications from heat-resistant polymers to medical applications. The electronic structure of these compounds is best described by Wade-Mingos rules for cluster molecules. Another important carborane is carborane acid, a chlorinated superacid $H(CHB_{11}Cl_{11})$, which has an anion structure shown at right.



Ball-and-stick model of *o*-carborane



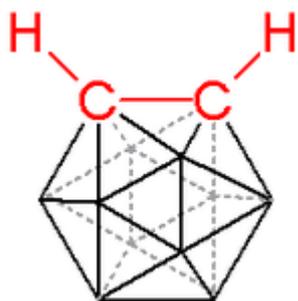
Ball-and-stick model of the carborane acid anion $[\text{CHB}_{11}\text{Cl}_{11}]^-$ (acidic proton not displayed)

Dicarbododecaborane

The most heavily studied carborane is $\text{C}_2\text{B}_{10}\text{H}_{12}$, m. p. $320\text{ }^\circ\text{C}$. It is often prepared from the reaction of acetylene with decaborane. A variation on this method entails the use of dimethyl acetylenedicarboxylate to give $\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2\text{C}_2\text{H}_5)_2$, which can be degraded to the $\text{C}_2\text{B}_{10}\text{H}_{12}$.

History.

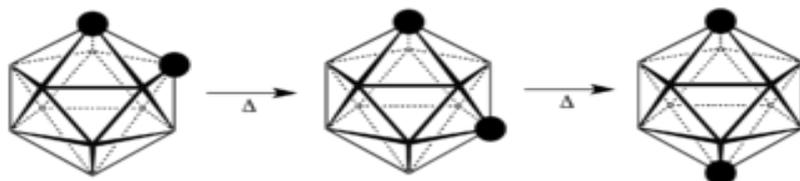
The 1,2-closo-dicarbododecaboranes (usually simply called carboranes), were reported simultaneously by groups at Olin Corporation and the Reaction Motors Division of Thiokol Chemical Corporation working under the U.S. Air Force and published in 1963.^[4] Heretofore, decaborane derivatives were thought to be thermally unstable and reactive with air and water. These groups demonstrated the unprecedented stability of the 1,2-closo-dodecaborane group, presented a general synthesis, described the transformation of substituents without destroying the carborane cluster, and demonstrated the ortho to meta isomerization.



skeletal formula of *o*-carborane, hydrogen atoms connected to boron omitted for clarity

Isomerization of dicarboranes.

Ortho dicarborane is the kinetic product from the addition of acetylenes to decarborane precursors. Upon heating at 420 °C, the ortho dicarborane rearranges to the meta isomer. Upon further heating, one obtains para-carborane. Like arenes, carboranes also undergo electrophilic aromatic substitution.



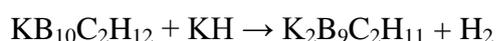
Thermal rearrangement of *o*-dicarborane to its meta- and para-isomers (CH vertex indicated with black spheres).

Dicarbollide

Numerous studies have been made on derivatives of the so-called dicarbollide anion, $[\text{B}_9\text{C}_2\text{H}_{11}]^{2-}$. The first metal dicarbollide complex was discovered by M. Frederick Hawthorne and co-workers in 1965.^[5] This anion forms sandwich compounds, referred to as bis(dicarbollides), with many metal ions and some exist in otherwise unusual oxidation states. The dianion is a nido cluster prepared by degradation of the parent dicarborane. For many practical syntheses, the monoprotonated dicarbollide salt $\text{B}_9\text{C}_2\text{H}_{12}^-$ is isolated as its potassium salt:^[6]



The monopotassium salt can then deprotonated with strong base:

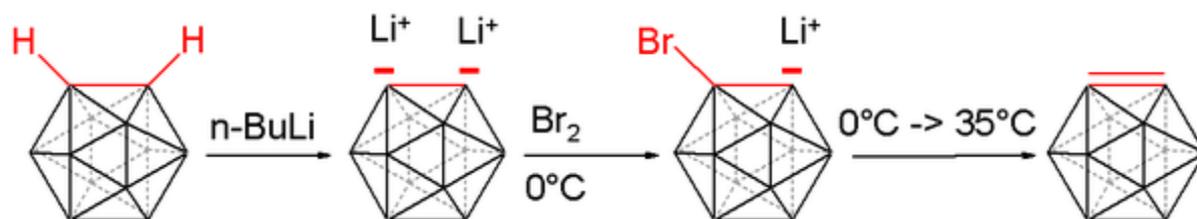


Bis(dicarbollides) often exhibit properties very different from their metallocene surrogates. For example, Ni-based bis(dicarbollide) cluster can be observed for the rare Ni(IV) oxidation state of nickel. Some notable examples of potential applications of these complexes include catalysis, ion-exchange materials for radioactive waste management, biologically active protease inhibitors, and chemically inert redox shuttles for dye-sensitized solar cells (DSSCs).

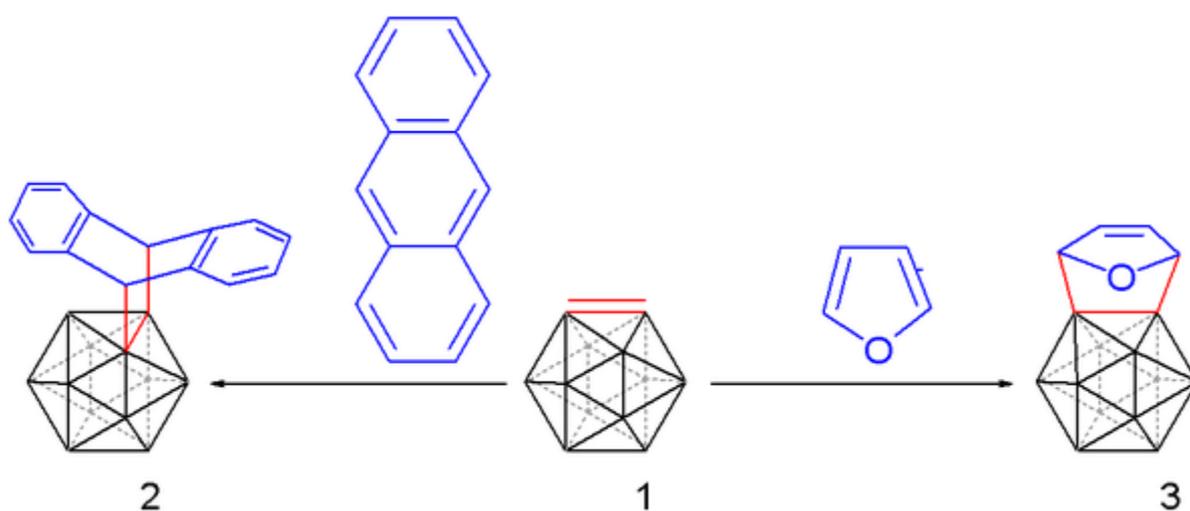
Carborynes

Carboryne, or 1,2-dehydro-*o*-carborane, is an unstable derivative of ortho-carborane with the formula $\text{B}_{10}\text{C}_2\text{H}_{10}$. The hydrogen atoms on the C2 unit in the parent *o*-carborane are

missing. The compound resembles and is isolobal with benzyne. A carboryne compound was first generated in 1990 starting from *o*-carborane. The hydrogen atoms connected to carbon are removed by *n*-butyllithium in tetrahydrofuran and the resulting lithium dianion is reacted with bromine at 0 °C to form the bromo monoanion.



Heating the reaction mixture to 35 °C releases carboryne, which can subsequently be trapped with suitable dienes:



such as anthracene (to afford a triptycene-like molecule) and furan in 10 to 25% chemical yield.

Carborynes react with alkynes to **benzocarboranes** in an adaptation of the above described procedure. *o*-carborane is deprotonated with *n*-butyl lithium as before and then reacted with dichloro-di(triphenylphosphino) nickel to a nickel coordinated carboryne. This compound reacts with 3-hexyne in an alkyne trimerization to the benzocarborane.

