

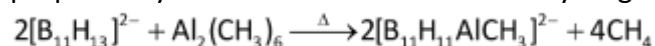
Crack CSIR-NET 2021

(Study Notes on
Metallaboranes and
Carboranes)



Metallaboranes and Carboranes

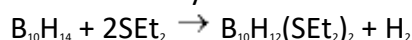
Metallaboranes are metals that contain B clusters. In some cases, metal is bonded to a borohydride ion through hydrogen bridges. Generally, more robust groups of Metallaboranes have direct meta-boron bonds. An example of Metallaborane is $\text{closo-[B}_{11}\text{H}_{11}\text{AlCH}_3\text{]}^{2-}$ which is prepared by the interaction of the acidic hydrogens in $\text{Na}_2[\text{B}_{11}\text{H}_{13}]$ with trimethylaluminum:



When B_5H_9 is heated with $\text{Fe}(\text{CO})_5$, a metalated analogue of pentaborane is formed. Boranes are very reactive to metal reagents due to which an attack can take place at several points on a polyhedral cage.

Carboranes is a large family of clusters which contain both C and B atoms.

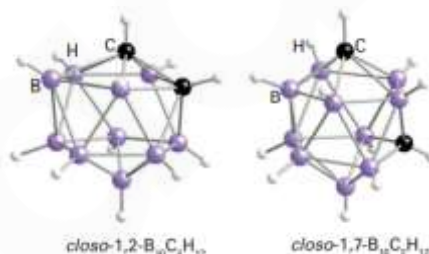
One of the interesting reactions of carboranes is the conversion of decaborane (14) to $\text{closo-1,2-B}_{10}\text{C}_2\text{H}_{12}$. The first reaction in this preparation is the displacement of H_2 molecules from decaborane by a thioether:



The loss of two H atoms in this reaction will be compensated by the donation of electron pairs by the added thioethers, so the electron count will remain unchanged. The product of the reaction is then converted to the carboranes by the addition of an alkyne:



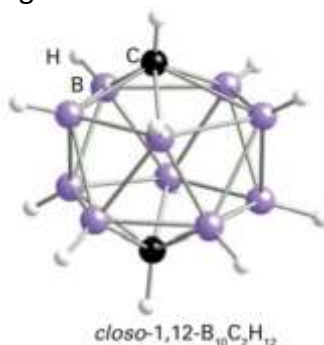
The four π electrons of ethyne will displace two thioether molecules (two two-electron donors) and an H_2 molecule (which leaves with two additional electrons). The net loss of two electrons correlates with the change in structure from a nido starting material to the closo product. The C atoms are in adjacent (1, 2) positions indicating their origin from ethyne. This closo-carborane survives in air due to which it can be heated without decomposition. At 500°C , in an inert atmosphere, it undergoes isomerization into $1,7\text{-B}_{10}\text{C}_2\text{H}_{12}$ (35), which in turn isomerizes at 700°C to the 1,12- isomer.



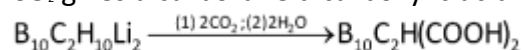
The H atoms attached to carbon in $\text{closo-B}_{10}\text{C}_2\text{H}_{12}$ are very mildly acidic, as a result, it is possible to lithiate these compounds with butyllithium:



These dilithiocarboranes are good nucleophiles and undergo many of the reactions that are characteristic of organolithium reagents

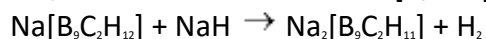
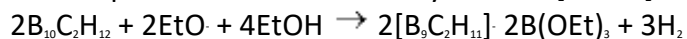


Thus, a wide range of carborane derivatives can be synthesised. For example, reaction with CO_2 gives a carborane dicarboxylic acid:

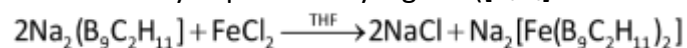


Similarly, I_2 leads to the diiodocarboranes and COCl yields $\text{B}_{10}\text{C}_2\text{H}_{10}(\text{NO})_2$.

Although $1,2\text{-B}_{10}\text{C}_2\text{H}_{12}$ is very stable, the cluster can be partially fragmented in strong base, and then deprotonated with NaH to yield nido $[\text{B}_9\text{C}_2\text{H}_{11}]^{2-}$:



The importance of these reactions is that nido- $[\text{B}_9\text{C}_2\text{H}_{11}]^{2-}$ is an excellent ligand. In this role, it mimics the cyclopentadienyl ligand ($[\text{C}_5\text{H}_5]^-$) which is widely used in organometallic chemistry:



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