

## DFT and *ab initio* studies of the addition step of alkyne bromoboration II

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An interesting feature of alkyne bromoboration is that the reaction of BBr<sub>3</sub> with acetylene provides an *anti*-adduct whereas reactions of BBr<sub>3</sub> with all other alkynes tested provide *syn*-adducts. This observation can be explained via a polar mechanism involving a direct addition of BBr<sub>3</sub> under the participation of Br<sup>-</sup> anion into the anti-arrangement [1]. The second possibility is a radical mechanism involving an addition of BBr<sub>3</sub> on the vinyl bromide radical. The second mechanism involves a very interesting intermediate. Both these possibilities are explored throughout our study. By means of *ab initio* calculations, we model the interaction between BBr<sub>3</sub> and acetylene in the presence as well as absence of Br<sup>-</sup> anion and the interaction of BBr<sub>3</sub> and vinyl bromide radical. Similar studies are performed for the cases of acetylene bromo-, chloro- and iodoboration. The guesses of all transition states are estimated using the single coordinate driving method. These guesses are then optimized and followed by the frequency analysis to verify the optimized transition states. All calculations are carried out at the B3LYP or MP2 level of theory as implemented in the Gaussian09 quantum chemical software. The mechanism is studied in the presence of CH<sub>2</sub>Cl<sub>2</sub> using SCRF model of implicit solvent.

[1] Semrád, H.; Stošek, J.; Munzarová, L. M. *Ab initio* studies of the acetylene bromoboration mechanism. *Conference abstract*, 52<sup>nd</sup> Symposium on Theoretical Chemistry – Chemistry in Solution, Bochum, Germany, **2016**.