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

Jakub Stošek[1] and Markéta L. Munzarová[1].
[1]*Department of Chemistry, Faculty of Science, Masaryk University. Kotlářská 2, CZ-611 37 Brno*

Even though alkyne bromoboration reaction is used by synthetic organic chemists since 1963, a theoretical study of Wang and Uchyama from 2012 [1] is the only theoretical analysis of its mechanism. An interesting feature of alkyne bromoboration is that the reaction of $BBr_3$ with acetylene provides an *anti*-adduct whereas reactions of $BBr_3$ with all other alkynes tested provide *syn*-adducts. Wang and Uchyama explain this observation via a subsequent isomerization of the *syn*-adduct promoted by another $BBr_3$ molecule. Their theoretical hypothesis is, however, in contradiction with experimental mechanistic studies of Jan Polášek and Ctibor Mazal from 2014 [2]. At the same time, the latter experimental study suggested a possibility of an alternative mechanism, involving a direct addition of $BBr_3$ under the participation of $Br^-$ anion into the anti-arrangement. This possibility is explored throughout our study. By means of *ab initio* calculations, we model the interaction between $BBr_3$ and acetylene in the presence as well as absence of $Br^-$ anion. 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 vacuum as well as in the presence of $CH_2Cl_2$. The calculations for molecules in $CH_2Cl_2$ are provided using SCRF model of implicit solvent [3].

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