# **Mechanistic analysis of alkyne *trans*-haloboration: A DFT and MP2 study**

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The application of alkyne haloboration with boron trihalides is known to result in various rations of *cis*/*trans* isomers, depending on alkyne identity and reaction time. While the currently accepted mechanism of trans adduct formation assumes exlusively a *cis*/*trans* isomerization, in our recent communication[1] we discussed an alternative route suggested by experiment and supported by theoretical data. Here we report a thorough quantum chemical study of direct acetylene trans-haloboration considering both polar (X $\in $ {Cl, Br, I}) and radical (X = Br) mechanisms. In particular, we model the interaction between BBr3 and acetylene in the presence as well as absence of an additional Br– anion as well as the interaction of BBr3 and vinyl bromide or vinyl bromide radical. Bromine-bridged free radicals with Br attached either to boron or to the neighboring carbon are established as key intermediates.

[1] Polášek, J.; Paciorek, J.; Stošek, J.; Semrád, H.; Munzarová, M. L.; Mazal, C. Stereoselective Bromoboration of Acetylene with Boron Tribromide. A Simple Preparation of (Z)-Bromovinylboronates. to be submitted to *J. Am. Chem. Soc.* **2020**.