

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 ratios of *cis/trans* isomers, depending on alkyne identity and reaction time. While the currently accepted mechanism of *trans* adduct formation assumes exclusively 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 ($X \in \{\text{Cl}, \text{Br}, \text{I}\}$) and radical ($X = \text{Br}$) mechanisms. In particular, we model the interaction between BBr_3 and acetylene in the presence as well as absence of an additional Br^- anion as well as the interaction of BBr_3 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**.