

DFT Studies on Mechanism and Reactivity of Radicals generated from Boronic Esters

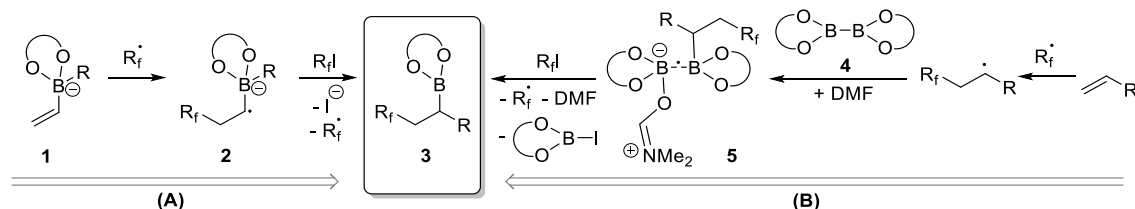
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Recently, new synthetically useful radical reactions involving the boronic ester group $-B(OR)_2$ have been developed. The addition of two alkyl groups (R , R_f) to a vinyl group can be achieved starting from vinyl boronic esters in a radical-polar crossover process (**A**).[1] Similar products (**3**) are obtained in the reaction of bis(catecholato)borane **4** with a radical formed by the addition of $\cdot R_f$ to substituted alkenes (**B**)[2]. Both mechanisms regenerate the initial radicals and the reactions are thus conducted as chain processes. In the absence of an alkene, the reaction of bis(catecholato)borane with a radical allows the metal-free borylation of alkyl and aryl iodides.[3]



We have conducted DFT studies on the mechanism of these reactions and discuss the reactivity and characteristic properties of radical intermediates such as **2** and **5**. The latter adduct (**5**) is remarkable as it contains a boron-boron one-electron σ bond and is stabilized by a solvent molecule (Figure 1).[2]

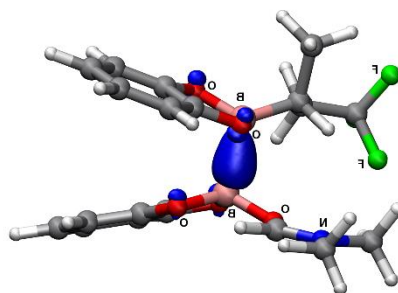


Figure 1: Spin Density Distribution (0.02 a.u.) of Radical **5** (PBE0/def2-TZVP)

References

1. M. Kischkewitz, K. Okamoto, C. Mück-Lichtenfeld, A. Studer, *Science* **355** (2017), 938.
2. Y. Cheng, C. Mück-Lichtenfeld, A. Studer, *J. Am. Chem. Soc.* **140** (2018), 6221.
3. Y. Cheng, C. Mück-Lichtenfeld, A. Studer, *Angew. Chem. Int. Ed.* **57** (2018), 16832.