XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Computational Investigation of Ligand Influence on the Insertion of Allene into Cu-B (Boryl) Bond

Ana Paula de Lima Batista, Ataualpa A. C. Braga

Departamento de Química Fundamental, Instituto de Química, São Paulo, São Paulo 05508-000, Brazil

Abstract: Borylation of unsaturated compounds catalyzed by transition metal boryl complexes have attracted increasing attention because the reactions yield organoboron derivatives that are used in synthetic processes, especially cross-coupling reactions [1,2]. Recently, Tsuji and co-authors reported, for the first time, the copper catalyzed boraformylation of allenes [1]. In this experimental study, they found that copper complexes bearing different ligands lead to huge discrepancies in the relative yields of β-boryl β,γ-unsaturated aldehydes. A crucial step of the general mechanism of this type of reaction involve the substrate insertion into the Cu-B (boryl) bond, which is usually responsible for the regioselectivity of the reaction [3]. In order to unveil the role of different ligands in the mechanism, the present work uses computational approaches to explore their influence on the insertion of allene into Cu-B (boryl) bond. Figure 1 shows the transition state (TS) associated with this process, in which a N-heterocyclic carbene ligand (NHC) is present. This TS was obtained at the B3LYP-D3/6-31G(d),SDD(Cu) level of theory using Gaussian09. Further DLPNO-CCSD(T) calculations and IBO (Intrinsic Bond Orbitals) analysis will be performed to refine energies and discuss bond interactions, respectively, on this system and others ones with different ligands.

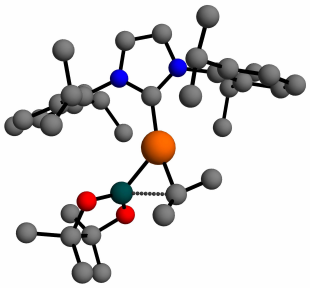

Figure 1. TS associated with the insertion of allene into Cu-B (boryl) bond. The H atoms are omitted for clarity.

Key-words: Boraformylation, Catalysis, DFT and CCSD(T) Calculations.
Support: This work has been supported by FAPESP, grants #2015/01491-3 and # 2014/25770-6

References:

[1] T. Fujihara, A. Sawada, T. Yamaguchi, Y. Tani, J. Terao, Y. Tsuji, Angew. Chem. Int. Ed. 56, 1539 (2017).
[2] E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, Todd B. Marder, *Chem. Rev.116*, 9091 (2016)
[3] H. Zhao, L. Dang, Todd B. Marder, Z. Lin *J. Am. Chem. Soc.,130*, 5586 (2008)