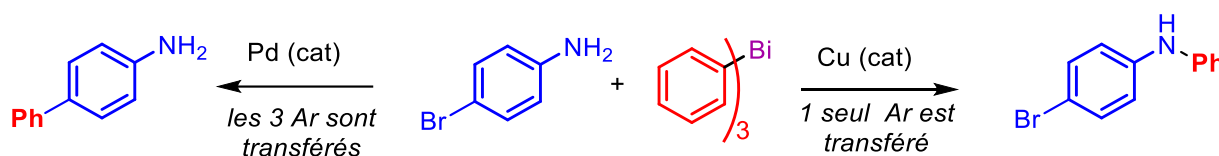
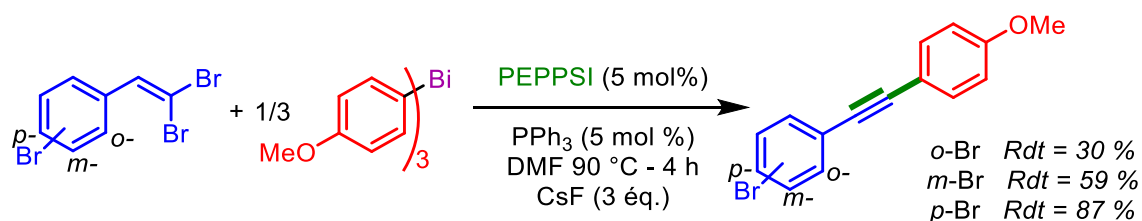


**Triarylbismuth as green crosscoupling reagent :
experimental versus theoretical mechanism insights**Christophe PICHON^a Sylvie CONDONAffiliations ^a ICMPE, Université Paris-Est Créteil (UPEC) 2 rue Henri Dunant 94 320 Thiais

Triarylbismuth are stable and easily prepared organometallic compounds. [1] Their main features come from this low toxic heavy metal (²⁰⁹Bi), trivalent with a slightly basic lone pair (*p*K_a ~5.2). These organometallics are efficient partners in metal-catalyzed crosscoupling reactions, mainly with copper or better with palladium where the 3 aryles are effectively transferred. [2] However this last reaction suffers from one side reaction: the dimer formation, which can be lowered using PEPPSI. [3]



The efficiency of these reactions is strongly dependent on the aryl substituents: electronic properties and relative position toward Bi atom. Furthermore, PEPPSI is robust enough to allow domino reaction involving an elimination/coupling/coupling process as described below.



A structure reactivity relationship study led from an experimental and theoretical point of view (DFT) pointed out a pretty classical Suzuki type mechanism for the aryl transfer, where the active species is an NHC-Pd-PPh₃. The rate determining step is the transmetalation's one which is even slower with an Ar₃Bi than an ArBiX than an ArBiX₂. Interestingly intramolecular chelation favors this step. [4,5]

References :

- [1] . Urgin, C. Aubé, C. Pichon, M. Pipelier, V. Blot, C. Thobie-Gautier, E. Léonel, D. Dubreuil, S. Condon *Tetrahedron Lett.* **2012**, 53, 1894 – 1896 [doi : 10.1002/chin.201231203]; [2]. S. Condon, C. Pichon, M. Davi *Org. Prep. Proced. Int.* **2014**, 46, 89 – 131 [doi: 10.1080/00304948.2014.884369]; [3] B. Cassirame, S. Condon, C. Pichon *J. Mol. Catal. A : Chem.* **2016**, 425, 2065 – 2078 [doi:]; [4] P. Kutudila, R. Linguerrri, C. Pichon, S. Condon, M. Hochlaf *Theor. Chem. Acc.* **2016**, 135, 1 – 10 [doi: 10.1007/s00214-016-1935-4] ; [5] .P. Kutudila, R. Linguerrri, M. Ponce-Vargas, C. Pichon, S. Condon, M. Hochlaf, *Molecular catalysis*, **2020**, 110649 [doi: 10.1016/j.mcat.2019.110649]

