THE REVISED MECHANISM OF COPPER-FREE SONOGASHIRA CROSS-COUPLING REACTION

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Palladium catalyzed alkynylation of aryl halides has become one of the most reliable methods for the construction of sp-sp2 carbon-carbon bond. [1] Although the first contributions of this cross-coupling date more than four decades ago, up to now, critical mechanistic questions remained unresolved.

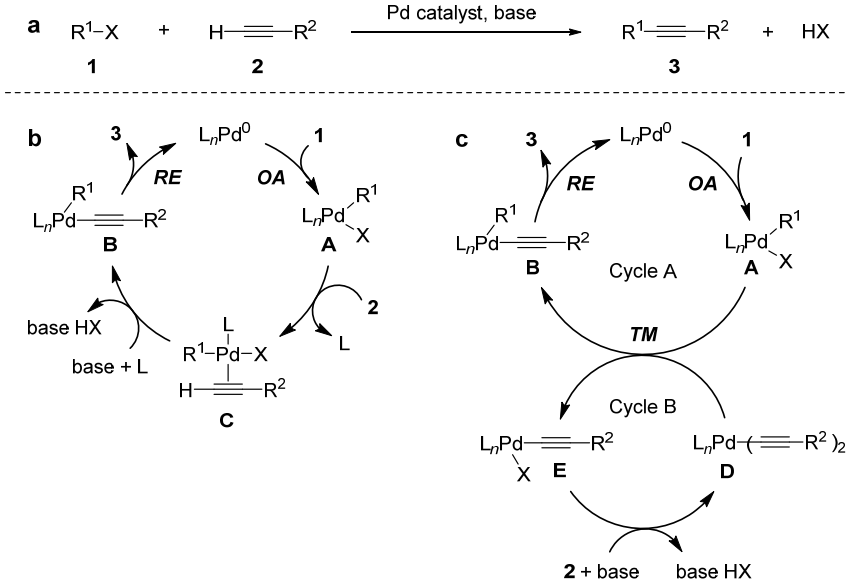

Figure 1. (a) General presentation of Cu-free Sonogashira reaction. (b) Texbook mechanism for Cu-free Sonogashira reaction. (c) Our mechanistic proposal for Cu-free Sonogashira reaction

Recently, experimental and computational scrutiny of the mechanism revealed, in contrast to the consensus mono-metallic mechanism, a transmetallation-centered tandem Pd/Pd catalytic cycle. [2, 3]

[1] de Meijere, A., Bräse, S. & Oestreich, M. (Eds). Metal Catalyzed Cross-Coupling Reactions and More (Wiley-VCH, Weinheim, Germany, 2014).

[2] M. Gazvoda, M. Virant, B. Pinter, J. Košmrlj, *Nat. Commun.* **2018**, *9*, 4814.

[3] M. Gazvoda, M. Virant, A. Pevec, D. Urankar, A. Bolje, M. Kočevar, J. Košmrlj, *Chem. Commun.* **2016**, *52*, 1571.