Université de Montréal, Montréal, QC, Canada

THIRD INTERNATIONAL SYMPOSIUM
ON C–H ACTIVATION

May 30 – June 2, 2016

OR03 – Intramolecular Pd-Catalyzed Dehydrogenative Allylations: Nucleopalladation *vs* Allylic C–H Activation

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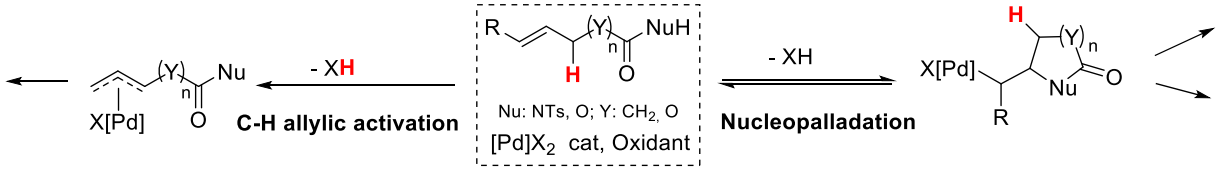
The oxidative intramolecular Pd(II)-catalyzed amination or oxylation of unsaturated N-sulfonyl carbamates,[1] N-sulfonyl carboxamides[1] and carboxylic acids[2] takes place through the involvement of cyclic aminopalladated or oxypalladated intermediates.[3]

These intermediates may subsequently evolve along different pathways such as distocyclic or proxycyclic[4] β-H elimination, oxidative oxylation, or intramolecular carbopalladation, as a function of the nature of the substrate and/or the reaction conditions. However, when the above reactivities are inhibited, the palladated intermediates are only off-cycle intermediates in equilibrium with the initial substrate. This hurdle opens the way to alternative oxidative cataytic cycles, the most relevant one being the C-H activation of the allylic position. Our experimental studies in concerto with DFT calculations[5] allow putting forward an unifying mechanistic scenario that rationalizes the ensemble of the observed results in this field.



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