Synthetic and Mechanistic Studies on the Pd-Catalyzed C(sp^3)–H γ-Arylation of Amino Acid Derivatives with Aryl Iodides

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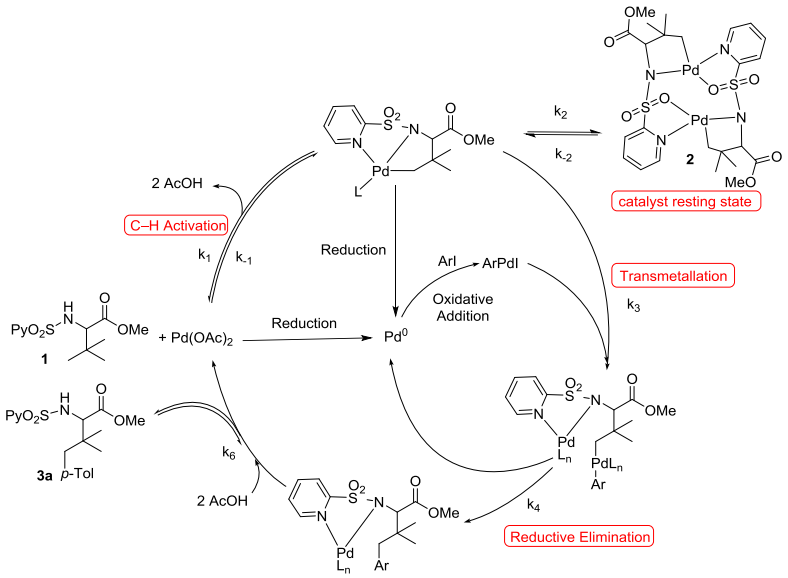
The seminar will describe the substrate scope and the mechanism of $Pd(OAc)_2$-catalyzed C(sp^3)–H γ–arylation of amino acids esters bearing a *N*-(2-pyridyl)sulfonyl directing group with aryl iodides.[1] A variety of *N*-(2-pyridyl)sulphonamide amino acid derivatives, including dipeptide substrates react with iodoarenes to furnish the γ-arylated products in synthetically useful yields and without racemization at the Cα center. Mechanistic investigations support that (*i*) the C–H activation step is reversible and it is not the turnover-limiting step, (*ii*) the bimetallic Pd(II) γ-metalated complex **2** is the resting state of the catalytic reaction and it is in equilibrium with an active monomeric species and (*iii*) a Pd(II)/(0) mechanism involving the transmetallation between two Pd(II) centers is operative.



These results might have a significant impact in the development of novel reactions in this field where a transmetallation between two Pd(II) centers might occurs as well as in future considerations in the mechanism of Pd-catalyzed C–H arylation reactions with aryl iodides, suggesting that a Pd(II)/(0) mechanism could be possible.

1. Rodríguez, N.; Romero-Revilla, J. A.; Fernández-Ibáñez, M. A.; Carretero, J. C. *Chem. Sci*, **2013**, *4*, 175-179.