Rhodium- and Iridium-Catalyzed Allylic Substitution with Unstabilized Nucleophiles

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The transition metal-catalyzed allylic substitution reaction is dominated by "soft" stabilized nucleophiles rather than "hard" unstabilized nucleophiles. This striking dichotomy can be ascribed to the high reactivity of the latter, which often promotes poor selectivity and unproductive reaction pathways. This seminar will outline the development of two unique transition metal-catalyzed allylic substitution reactions with challenging unstabilized nucleophiles. The first part will focus on the development of the regio- and diastereoselective rhodium-catalyzed allylic substitution with unstabilized benzyl nucleophiles to afford ternary benzyl motifs present in several medicinally important agents, e.g., Aliskiren, Indinavir *etc.* In contrast, the second part will outline the development of a novel regio- and enantioselective iridium-catalyzed allylic substitution reaction with Reformatsky reagents for the direct synthesis of enantioenriched ternary homoallylic esters, which represent key intermediates for the synthesis of γ -aminobutyric acid (GABA) family of drug molecules, e.g., Phenibut, Baclofen, Rolipram *etc.*

