Abstract

The thesis entitled "Heterobimetallic Catalysis within Palladium–Tin Domain: Carbon-Carbon & Carbon-Heteroatom Bond Formation" is primarily an effort towards the exploitation of the synthesis and catalytic activity of various heterobimetallic 'Pd–Sn' complexes towards different types of organic transformations leading to carbon– carbon and carbon–heteroatom bond formation. Heterobimetallic 'Pd–Sn' complexes, having direct Pd–Sn bonds namely PdCl(COD)SnCl₃, PdCl(PPh₃)₂SnCl₃, and Pd(dppe)(SnCl₃)₂.were easily synthesized by the insertion reaction of SnCl₂ across lowvalent late transition metal (TM) complex bearing a 'Pd–Cl' unit, in presence of ligand in acetone-dichloromethane at room temperature. The work is described in mainly four parts which are summarized below.

We delineate a new heretobimetallic 'Pd–Sn' catalysis concept to activate differently substituted enones towards an efficient Michael addition reaction with different carbon (arene, heteroarene, 1,3-dicarbonyl compound), sulfur (thiol), oxygen (alcohol), and nitrogen (amine) nucleophiles. Spectroscopic investigations showed the *in-situ* generation of bimetallic 'Pd-Sn' species as well as the dual activation of enone. We also performed PdCl(COD)SnCl₃ catalyzed facile and selective substitution reaction of π -activated alcohols like benzyl, allyl and propargyl alcohols with different types of C-nucleophiles. From in situ¹H NMR studies, we tentatively conclude that the pre-activation of the alcohol involves initial coordination of the alcoholic -OH group to oxophilic 'Pd-Sn' catalyst. The plausible mechanism of alkylation and the intermediacy of ether have been enumerated. Also the plausible intermediacy of ether prompted us to study successfully the prospect of ethers as alkylating agents. In continuation with the objective of the thesis, an efficient and highly atom-economical intermolecular hydroarylation of electron-rich α -methyl substituted aryl alkenes with indoles and other heretoarenes nucleophiles was also demonstrated using the PdCl(COD)SnCl₃ catalyst under moisture and air insensitive conditions. The addition reaction is also highly regioselective and in all cases only Markovnikov products are obtained. Next, a simple method to synthesis of indeno[2,1-b]thiophene and indeno[1,2-b]indole motifs by heterobimetallic 'Pd–Sn' catalysed formal three-component coupling, involved a Suzuki reaction followed by nucleophile assisted tandem ring closure has been described.

Keywords: Heterobimetallic, Palladium, Tin, Insertion, Catalyst, Michael Addition, Allylation, Benzylation, Propargylation, Hydroarylation, Tandem Ring Closing.