

Abstract

The thesis entitled “**Electrophilic Activation across a Multimetallic Piano-Stool Iridium-Tin Catalyst: Synthetic and Mechanistic Studies**” is primarily an effort towards the synthesis, characterization and catalytic activity of a newly designed multimetallic piano-stool complex $\text{Cp}^*\text{Ir}(\text{SnCl}_3)_2\{\text{SnCl}_2(\text{H}_2\text{O})_2\}\cdot 3\text{H}_2\text{O}$ (here after abbreviated as Ir–Sn₃). The work is described in mainly three parts which are summarized below.

The multimetallic complex $\text{Cp}^*\text{Ir}(\text{SnCl}_3)_2\{\text{SnCl}_2(\text{H}_2\text{O})_2\}\cdot 3\text{H}_2\text{O}$ was easily synthesized by the insertion reaction of SnCl_2 across the Ir–Cl bonds of $[\text{Cp}^*\text{IrCl}_2]_2$ in refluxing 1,2-dichloroethane. Upon slow diffusion of *n*-hexane to the dichloroethane solution, the product Ir–Sn₃ crystallized out as greenish yellow blocks in good yield. The Ir–Sn₃ complex was well characterized by crystallographic, NMR spectroscopic techniques as well as by elemental analysis. Inter- and intramolecular α -amidoalkylation reactions were successfully carried out by this Ir–Sn₃ complex. In this context, phthalimide and succinimide derived γ -hydroxylactams were activated by Ir–Sn₃ complex to generate *N*-acyliminium ion intermediates which were effectively trapped by an array of nucleophiles (arenes, heteroarenes, 1,3-dicarbonyls, allyltrimethylsilanes, sulfonamides, alcohols, thiols etc.) inter as well as intramolecularly to synthesize important organic skeletons like bicyclic γ -lactams. More importantly we applied this methodology towards the synthesis of indolizidine skeletons. We also found that γ -hydroxylactams obtained from succinimide could lead to eliminated or substituted products depending mainly on reaction parameters like catalyst loading and time. It was apparent from the observations that in our reaction conditions the eliminated product was kinetically controlled while substituted product was thermodynamically controlled. A tandem endocyclic *N*-acyliminium ion formation/oxocyclization/exocyclic *N*-acyliminium ion formation/ π -cationic cyclization cascade was observed particularly in the cyclization of *N*-aryloxymethylamidals in presence of Ir–Sn₃ catalyst. Some controlled experiments suggested that Ir–Sn₃ catalyzed α -amidoalkylation reactions were proceeded via S_N1-type pathway through the intermediacy of *N*-acyliminium ions. We also performed the substitution reaction of π -activated alcohols like benzyl, allyl and propargyl alcohols with different types of nucleophiles. An interesting observation was recorded for the reaction of 3° propargyl alcohols with 1,3,5-trimethoxy benzene (a bulky arene) which lead to unexpected indenenes instead of normal propargylated products. It was found that the reason behind this unusual transformation is purely steric in nature. A Hammett correlation study was also carried out for the likelihood of electrophilic bond activation model in the substitution reaction of π -activated alcohols.

Keywords: Multimetallic, Iridium, Tin, Insertion, Catalyst, Alpha-Amidoalkylation, Gamma-Hydroxylactam, Bicyclic Gamma-Lactam, Benzylation, Allylation, Propargylation, Indene, Electrophilic.