

Abstract

The thesis entitled “**Carbon-Carbon and Carbon-Heteroatom Bond Activation via Silver(I) Catalysis: Synthetic and Mechanistic Studies**” is primarily an effort towards the exploitation of the catalytic activity of silver(I) diene complexes. The results are described in mainly three chapters. The abstract of each chapter are given below.

Silver(I) complex $[\text{Ag}(\text{diene})_2]^+\text{Y}^-$ (where diene = cyclooctadiene, norbornadiene, and 1,3-cyclohexadiene; $\text{Y}^- = \text{PF}_6^-, \text{BF}_4^-$) efficiently catalyzes the arylation of *N*-tosyl aziridines with arenes and heteroarenes under ambient condition to provide the corresponding β -aryl amine derivatives with excellent regioselectivity. To understand the nature of substrate activation, and initial bond breaking/making steps, the following studies were conducted with the help of *in situ* NMR (^1H , ^{31}P , ^{109}Ag) and ESI-MS probe: (I) evaluation of Hammett reaction constant (ρ); (II) correlation of initial rate (k) versus cone angle (θ) of ligand L for reactions mediated by $[\text{Ag}(\text{COD})_2]\text{PF}_6/\text{L}$ (where L is a phosphine or a phosphite ligand); (III) identification of silver-arene intermediates in solution; (IV) correlation of initial rate (k) with $\Delta_{\text{HOMO-LUMO}}$ of $[\text{Ag}(\text{diene})_2]\text{PF}_6$ obtained from preliminary DFT studies. Study-I led to a ρ -value of -0.586 , indicating that the extent of electrophilic perturbation is considerably less than a typical Lewis-acid catalyzed process. Study-II indicated that initial rate (k) increases with concomitant increase in θ , as well with $\Delta^{31}\text{P}_{(\text{complex-ligand})}$ which corroborates to a mechanism involving prior ligand-dissociation. Study-III showed the plausible formation of $[\text{Ag}(\text{diene})(\text{arene})]^+$ and $[\text{Ag}(\text{arene})_2]^+$ as reactive species in solution. Study-IV showed that the dependence of initial rate (k) with diene ligand is in the order $\text{COD} > \text{NBD} > \text{CHD}$; which corresponds well with the order of hardness of the respective Ag(I)-complexes.

$[\text{Ag}(\text{COD})_2]\text{PF}_6$ catalyzes the reaction between propargyl alcohols and *N*-tosylaziridines/azetidines leading to a diverse range of N,O-heterocycles namely oxazines, oxazepines and oxazocines via ring opening and closing in a cascade. In mechanistic details, a proposal on the reaction course is presented through two different catalytic event operating in cascade. The initial event will involve activation of the heteroatoms of the substrates by $[\text{Ag}(\text{COD})]^+$. This will facilitate the opening of the aziridine/azetidine ring. π -activation and metallotropic rearrangement of ring-opening product is expected to result in the formation of intermediates Ag(I)-alkyne, and Ag(I)-allene. When assisted by a base, the ring-closing event

from Ag(I)-alkyne, and Ag(I)-allene may follow *endo-dig* or *exo-dig/trig* pathways – subsequent protodemetalation would afford the organic product and regenerate the Ag(I) catalyst. In that case cyclization goes through *endo*-selective manner.

Effective and regioselective ring opening of *N*-tosylaziridines was conducted by 2 mol% $[\text{Ag}(\text{COD})_2]^+\text{Y}^-$ (Y= PF_6 , BF_4) in dichloroethane at ambient temperature. Various types of nucleophiles, such as alcohols, amines and thiols could open the strained aziridines molecules to produce corresponding 1,2-vicinal amino ether, diamine and amino thioether in high yields. Subsequently we have attempted the ring-opening of aziridines with tethered dinucleophile. The kinetic study for the reaction of 2-phenyl *N*-tosylaziridine with representative O, N, S nucleophile namely phenol, aniline and thiophenol were carried out in presence of 2 mol % $\text{Ag}[(\text{COD})_2]\text{PF}_6$. The results indicated that the reactivity is in the order $\text{SH} > \text{OH} > \text{NH}_2$.