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A Brief Review on Silver Complexes of Functionalized N-heterocyclic Carbene Ligand

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Abstract: NHC Carbenes are better sigma donor than their phosphines counterpart and the importance of structure variation in the carbene backbone is the key in utilising the silver complexes of these NHC ligands play a crucial role in today's chemistry. Some of the recent catalytic transformations has been reviewed.

Keywords: N-heterocyclic Carbene (NHC), Organometallic Chemistry, Coordination Chemistry.

I. INTRODUCTION

The N-heterocyclic carbenes are now dominating the field of organometallic and inorganic coordination chemistry in the area of catalytic applications.[1]

The increasing attention is primarily because of their ability to act as good spectator ligands in a variety of transition metal complexes all the while influencing their catalytic properties and also for their ability to act as nucleophilic reagents and as catalysts in diverse organic transformations.[2]

The N-heterocyclic carbene compounds exhibit good compatibility with heteroatom bearing functional groups and are air and moisture stable, thereby overall broadening the scope of their applicability in numerous organic transformations.[3]

II. STRUCTURAL DIVERSITY AMONG THE TRANSITION METAL COMPLEXES OF N-HETEROCYCLIC CARBENES

Various types of weak log-range interactions like the hydrogen-bonding interaction or the closed shell $d^{10}\cdots d^{10}$ "argentophilic" (Ag···Ag) interactions[i] play an important role in bringing about structural diversity[ii,iii] observed in the various silver complexes of N-heterocyclic carbenes.

From the simple monomeric and dimeric to the more complex oligomeric as well as the polymeric motifs displaying varied shapes and conformations are noticed among the silver complexes of N-heterocyclic carbene ligands.

The molecular aggregation in the Ag-NHC complexes results in various shapes and sizes ranging from helical[iv,v] to H-shaped[vi] to clusters.[vii] These compounds find utility as devices, like microelectronics and optoelectronics, as well as pharmaceutical materials,[viii,ix] and thereby making them important synthetic targets.

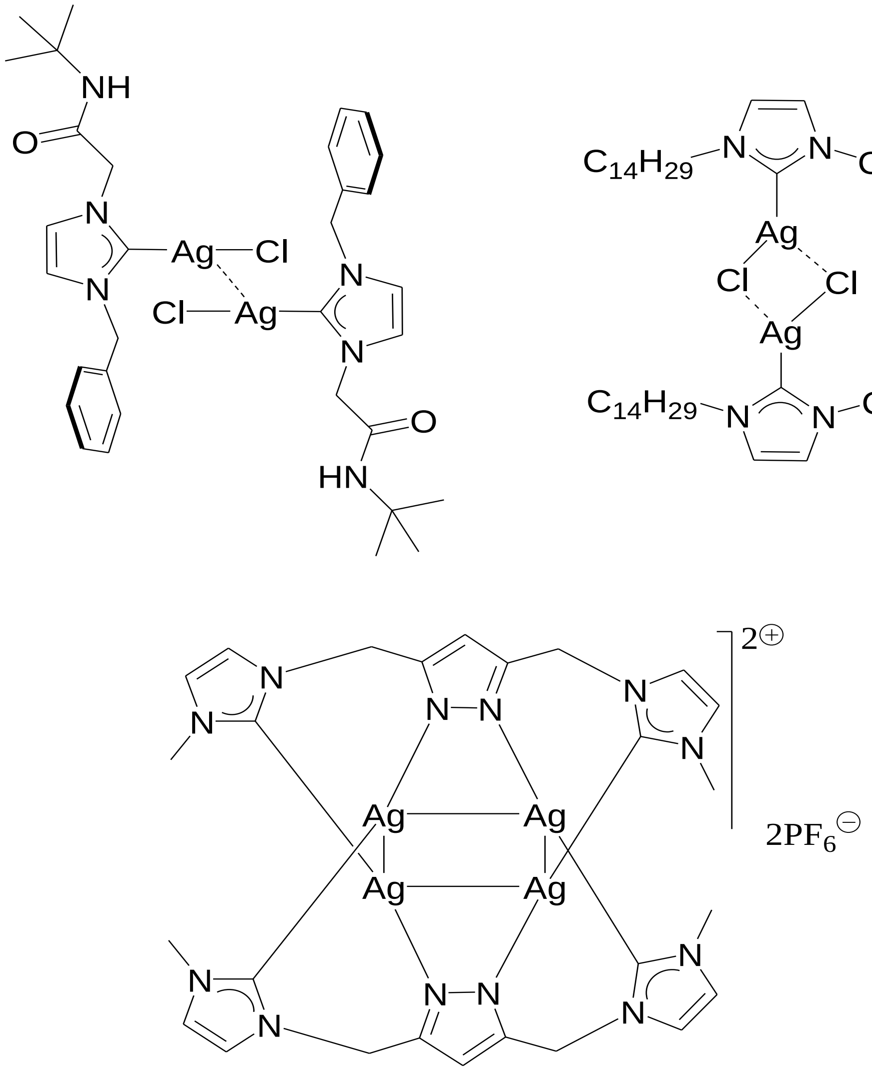

Figure 1

The “self assembly” methods have often been employed for generating complex structural motifs, however its main drawback resides with the lack of synthetic control. As a consequence various methodologies have been developed by modifying the sterics and electronics of the ligands as well as by varying the metal ion, solvent, template, counter-ions, etc.

An inherent advantage of N-heterocyclic carbenes lies in its convenience with ligand tunability through rational modification at nitrogen as well as on the carbon skeleton of the imidazole ring.[4] For example, steric tuning is achieved by putting in bulky groups on the nitrogen atom whereas the variation in the electronic effect is done by the changing the azole rings. For example on going from imidazole to triazole rings minimizes the electron donating power of the carbene centre in N-heterocyclic carbenes. Furthermore, the N-heterocyclic carbene bearing weakly coordinating labile functionalities allow reversible coordination to the metal centre that temporarily stabilize a catalyst species while at the same time allow substrate coordination and activation.[5] The electronic properties of the N-heterocyclic carbene ligands bear a striking resemblance to the phosphine ligands so much so that the N-heterocyclic carbenes are popularly termed as the phosphine substitutes. The decreased labiality coupled with high stability of the Nheterocyclic carbene complexes help stabilizes many important catalytically relevant species by prolonging its lifetime.[6]

Additionally, the overall topology of the N-heterocyclic carbene and the position of the N-bound substituents relative to the metal centre are such that it allows a large variation of the sterics and the electronics around the metal centre. Because of the tighter binding to the metal, the N-heterocyclic carbene catalysts do not show catalyst leaching to a great extent and also are robust to oxidations, which together prevent catalyst degradation in reactions performed under aerobic conditions.[7]

A key rationale guiding the design and synthesis of N-heterocyclic carbenes lies in stabilizing singlet carbene precursors. For the purpose various modifications have been performed by changing the sterics and electronics through incorporation of bulky substituents or by moving from rigid to hemi-labile to labile substituents to even changing the N-heterocyclic carbene ring sizes. The acidity of the carbene centre can directly be tuned on going across saturated imidazole to unsaturated imidazole to triazole to pyrazole to abnormal N-heterocyclic carbene scaffolds to meet the required activity and the geometry for a catalytic transformation. Recently, even acyclic N-heterocyclic carbene and borazine derived imidazoline carbene ligands have been synthesized.[8]

Silver N-heterocyclic Carbene complexes

The silver N-heterocyclic carbene complexes have largely attracted attention for its application as carbene transfer agents in the synthesis of various transition metal complexes.[9] This particular utility of silver primarily arises from its ease of formation of N-heterocyclic carbene complexes and from the ease with which it subsequently transfer the N-heterocyclic carbene ligands on to the other transition metals. This reaction is commonly called a transmetallation reaction. Apart from the aforementioned transmetallation route, the transition metal complexes of N-heterocyclic carbene ligands can also be prepared by using a strong base followed by the reaction with the desired metal precursor, commonly referred to as the direct deprotonation method.[10] However, the silver N-heterocyclic carbene based transmetallation route is more convenient than the direct deprotonation route. An additional advantage of the transmetallation reaction is that the silver N-heterocyclic carbene complexes, being air and moisture stable, the reaction can be conveniently performed under aerobic conditions and in some cases even in water.

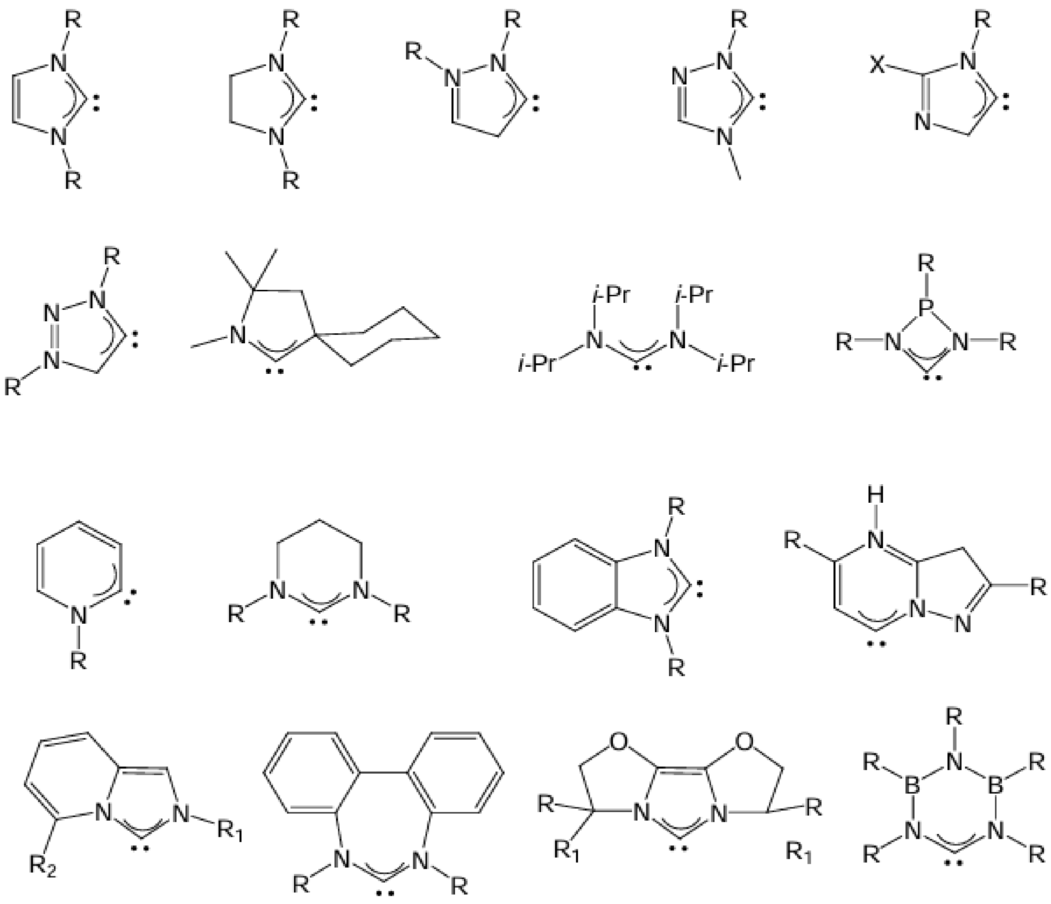

Figure 1. Structural and electronic variation in NHCs scaffolds.

Though largely used in transmetallation reactions, the utility of silver N-heterocyclic carbene complexes in chemical catalysis remained unexplored for long until recently. The first true utility of silver N-heterocyclic carbene complexes in catalysis was observed for the diboration of alkene at room temperature.[11] Specifically, $_{bis}$(catecholate)diboron reagent underwent reaction with internal or terminal alkenes in presence of 5 mol % of the silver catalyst, [(1-methyl-3-methylmenthoxide)$_2$Ag]AgCl$_2$, resulting in a diboron compound that was subsequently oxidized giving the corresponding diol compound.

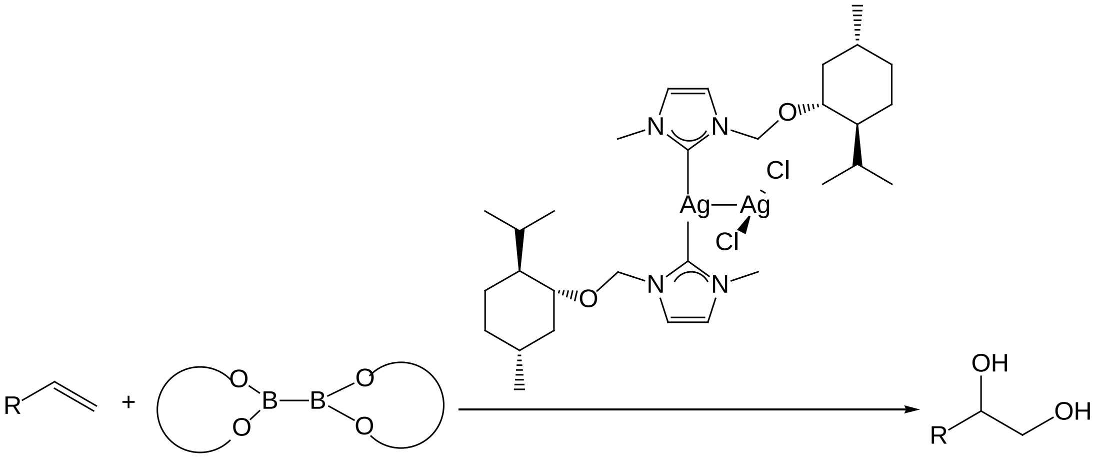

Figure 2. Silver N-heterocyclic carbene catalyzed diboaration of olefin.

Silver N-heterocyclic carbene complexes have shown promising activity in the ringopening polymerization (ROP) of L-lactide for synthesizing polylactide polymers.[12] The advantage of using polylactide polymer is that they are not only biodegradable but also the monomer can be generated from renewable resources such as by corn fermentation process or from agricultural starch wastes etc. Furthermore, due to their good mechanical property and biocompatibility, the polylactide polymers have found utility in medical and pharmaceutical applications.

Recently, our group has used silver N-heterocyclic carbene complexes for the ring opening polymerization of L-lactide under melt polymerization conditions.[13] Specifically, the [{1-*iso*propyl-3-(*N*-phenylacetamido)imidazol-2ylidene}$_2$Ag]$^+$Cl$^-$ complex catalyzed ring-opening polymerization of L-lactide at elevated temperatures under solvent-free melt conditions to give a polylactide polymer of moderate molecular weight with narrow molecular weight distribution.

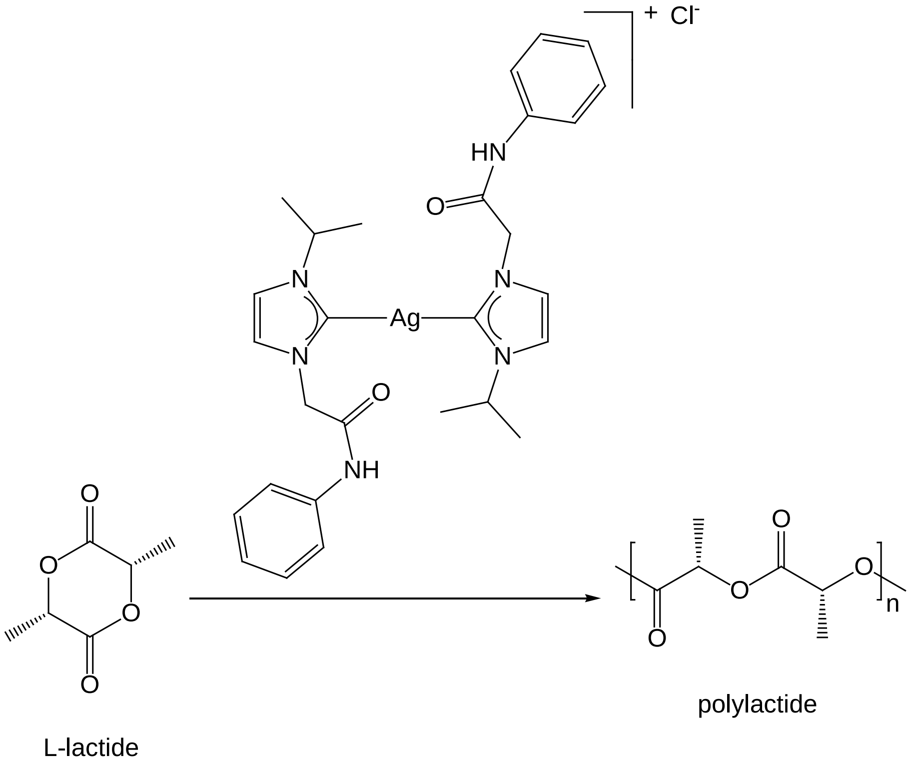

Figure 3. Silver N-heterocyclic carbene catalyzed ROP of L-lactide.

Ester to ester transformation through exchange of alcohols is commonly known as the transesterification reaction.[14] Though simple acid or base catalyzed transesterification reactions were long known, only recently the metal N-heterocyclic carbene complexes catalyzed transesterification reactions have gained prominence because they facilitate the reaction in thermodynamically unfavorable aqueous medium.

Specifically, the silver complex, [(1-ethyl-3-methylimidazol-2-ylidene)Ag]$AgCl_2$, catalyzed the reaction of methyl benzoate with ethyl alcohol to give the transesterification product. The ethyl benzoate and the free carbene trapped using CS_2 both generated in the reaction process, were analyzed by the NMR studies.

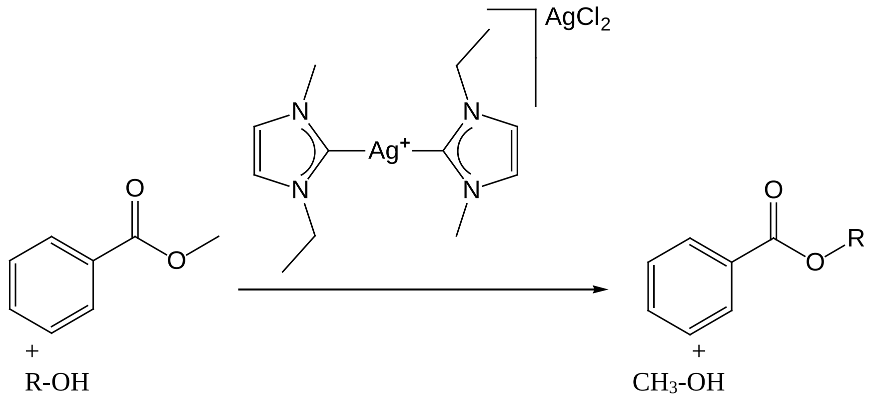

Figure 4. Silver N-heterocyclic carbene catalyzed transesterification reaction.

The silver N-heterocyclic carbene have been successfully applied in the atom economic hydrosilylation of olefins and alkynes.[15] For example, hydrosilylation of benzaldehyde with Me_2PhSiH catalyzed by the [1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene]AgCl complex, proceeded cleanly to yield the desired silyl ether product.

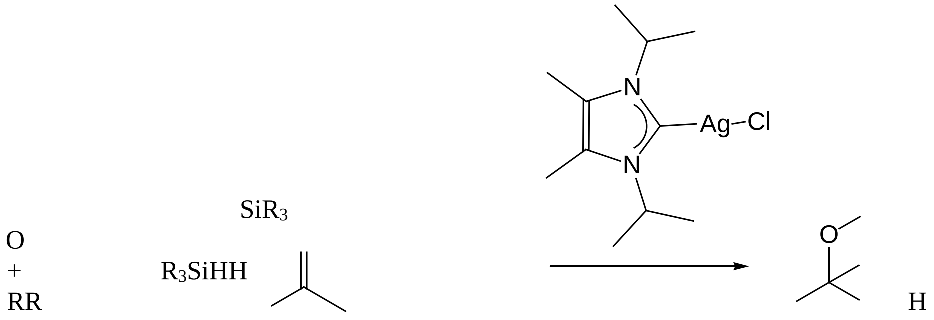

Figure 5. Silver N-heterocyclic carbene catalyzed hydrosilylation reaction.

A preliminary ethylene polymerization study employing a moderately active silver complex, [Ag(3-methyl-1-picolylimidazolin-2-ylidene)$_2$]$_3$I}I_2, has recently been reported.[16]

As polyolefin is the fastest-growing segment of the polymer industry, there is a constant need for designing and synthesizing new polymerization catalysts, as they play a major role in determining the activity and the stereo control of polymerization process.

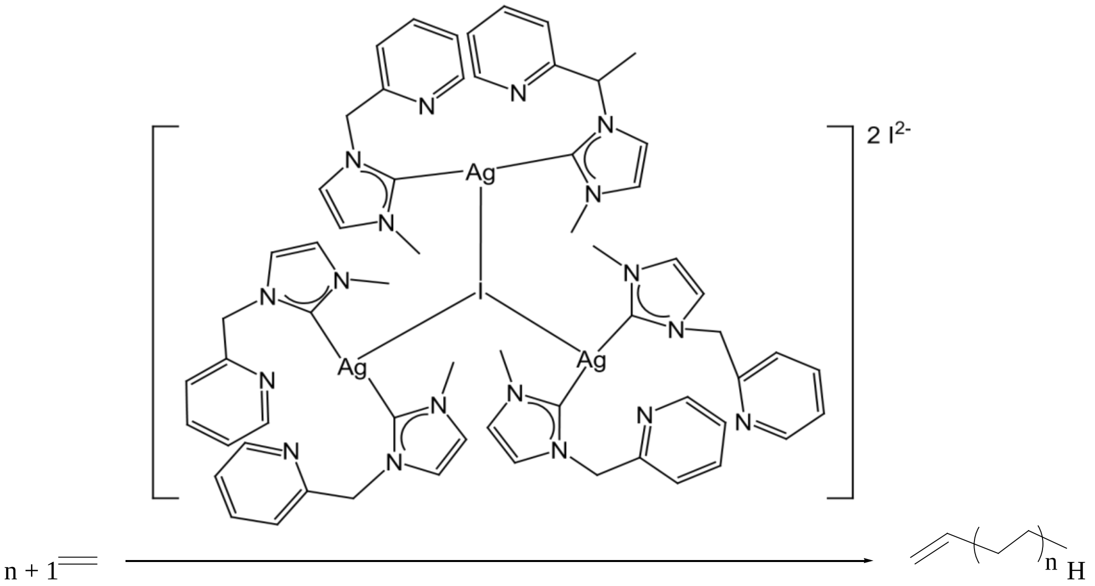

Figure 6. Silver N-heterocyclic carbene catalyst for olefin polymerization.

III. CONCLUSION

In summary, the designing and emerging better catalyst is a constant ongoing task in the organometallic chemistry, which can be fulfilled by understanding of nature of the metal N-heterocyclic carbene bond and the reaction mechanism using computational studies. The importance of the silver metal complexes of N-heterocyclic carbene ligands and their broad applications in chemical catalysis has been progressively increasing as can be seen from the above discussions of the utility of Ag complexes of N-heterocyclic carbene in homogenous catalysis.

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