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Palladium & Ruthenium Complexes Of Functionalized N-heterocyclic Carbene Ligand: A Brief Review

Dr. Sachin Kumar*

Department of Chemistry, Sanjay Gandhi (P.G.) College, Sarurpur Khurd, Meerut.

Abstract: Role of Metal on NHC Carbenes are crucial as the tuning of electronic and steric properties of carbene ligands is the deciding factor in the application of these metal and NHC ligands complexes. The comparison of NHC vs Phosphine based metal complexes is discussed and recent catalytic applications of palladium and ruthenium based NHC ligands are discussed in details.

Keywords: N-heterocyclic Carbene (NHC), Organometallic Chemistry, phosphine-substitutes, ancillary ligands

I. INTRODUCTION

Though the first transition metal complexes of N-heterocyclic carbene (NHC) ligands were reported by Öfele[i] and Wanzlick[ii] independently in 1968, the first stable "bottleable" free carbene could only be isolated much later in 1991 by Arduengo.[iii] This led to the beginning of a new era of N-heterocyclic carbenes as ancillary ligands for designing transition metal based catalysts. The NHCs are similar to the phosphines in terms of their electron-donating abilities and are gaining popularity as "phosphine-substitutes". Though both of these ligands possess strong □-donating abilities, the phosphines are better □-acceptors than the N-heterocyclic carbenes. It is worth noting that the stability of NHC-supported transition metal complexes has been found to be greater than the phosphine-supported ones. Traditionally, the phosphines are known as ligands in organometallic chemistry for a long time and consequently their transition metal complexes have found utility in various C-C cross coupling reactions, namely, Suzuki-Miyaura, Heck, Stille, Sonogashira, Kumada-Tamao-Corriu coupling reactions. However owing to their inherent unstable nature leading to catalyst leaching, the focus is gradually shifting towards the N-heterocyclic carbenes lately. Furthermore, the fact that the NHCs are poor □-acceptors, make them better □-donors than the phosphines. Hence the N-heterocyclic carbene complexes are increasingly preferred in those chemical transformations that require electron-rich metal centers. Thus over time, the N-heterocyclic carbenes have metamorphosized into an important class of ancillary ligands for various transition metal complexes. These transition metal complexes of N-heterocyclic carbenes have found a wide spread utility in hydrogenation,[iv] hydrogen transfer,[v] hydroformylation,[vi] hydrosilylation,[vii] isomerization,[viii] telomerization,[ix] Kharash addition,[x] Pauson-Khand cyclization,[xi] olefin metathesis[xii] and various C-C cross coupling reactions.[xiii] The biomedical applications of the transition metal complexes of N-heterocyclic carbene ligands are gradually emerging with numerous reports of their antitumor,[xiv] antimicrobial[xv,xvi] and antifungal properties[xvii] surfacing lately.

II. PALLADIUM N-HETEROCYCLIC CARBENE COMPLEXES

The overall impact of the palladium catalyzed C–C cross-coupling reactions, discovered in the 1970s, has been considerable and continues to be the focus of research.[30] Several palladium N-heterocyclic carbene complexes have been employed in a variety of C–C cross-coupling reactions.[31] For example, in a palladium catalyzed Heck reaction when 4bromotoluene was reacted with *t*-butyl acrylate in presence of [*N-N'bis*(methyl)imidazol-2-ylidine]$_2$Pd as a catalyst the desired product (E)-*t*-butyl 3-*p*tolylacrylate was obtained in a good yield.

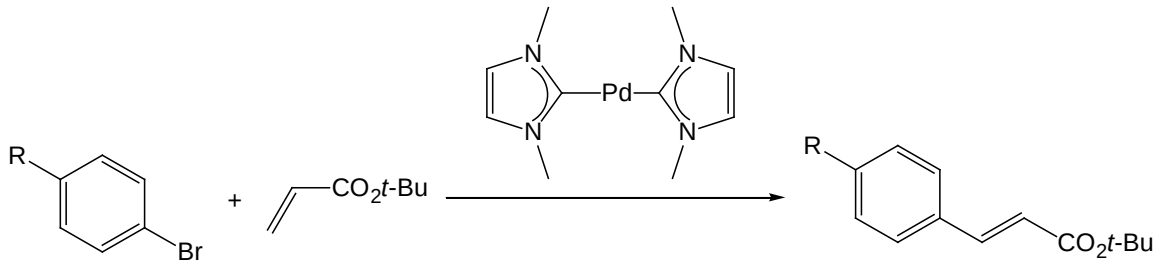

Figure 1. Palladium N-heterocyclic carbene catalyzed Heck cross-coupling reaction.

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Suzuki-Miyaura reaction is another cross-coupling reaction that has made a significant impact on the existing C–C bond forming methodologies currently used in organic synthesis.[32]

Attributes like mild reaction conditions, high functional group tolerance, stability of boronic acids to heat, oxygen, and water, the ease of handling and separation of boron containing byproducts from the reaction mixtures makes Suzuki-Miyaura crosscoupling a highly popular methodology.[33]

In this regard, notable is a *trans*-[1-(benzyl)-3(*N*-t-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl_2 complex that successfully catalyzed the Suzuki-Miyaura cross coupling of 2-bromobenzaldehyde to phenylboronic acid in good yield.

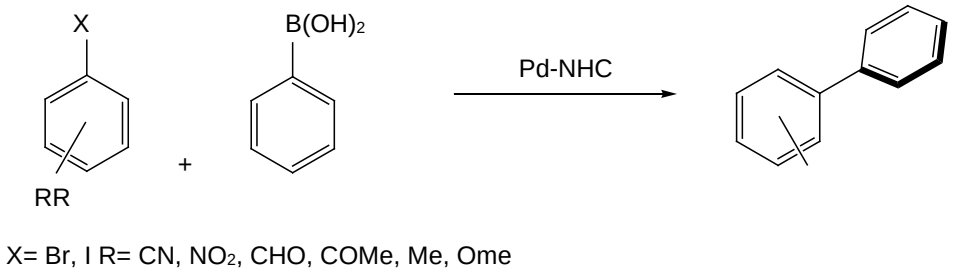

Figure 2. Palladium N-heterocyclic carbene catalyzed Suzuki-Miyaura cross-coupling reaction.

The oxidation of alcohols is an important reaction in organic synthesis and for which several palladium N-heterocyclic carbene complexes have been reported.[34]

For example, 1-phenylethanol was successfully oxidized to acetophenone, using molecular oxygen, in presence of catalytic amount of [(S)-1,1-(1,1-binaphthyl)-3,3-dimethyldibenzimidazo-2ylidene]PdI_2 complex.

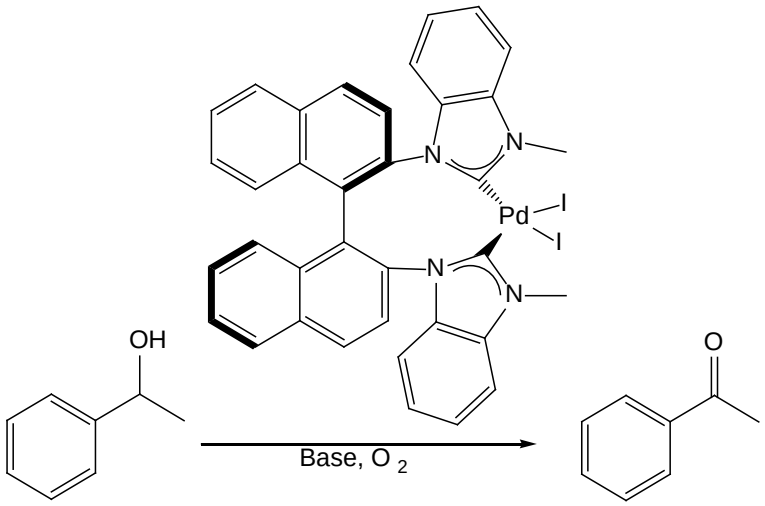

Figure 3. Palladium N-heterocyclic carbene catalyzed aerobic oxidation of alcohol.

The direct conversion of carbon−hydrogen bonds, better known as C−H activation, into carbon–hetero atom bonds remains a critical challenge in organic chemistry and which has found numerous applications in pharmaceuticals, natural products and polymers.[35]

Several palladium N-heterocyclic carbene complexes have exhibited C–H activation activity. For example, a suspension of potassium peroxodisulfate in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride at a methane pressure of 20 bar, in the presence of catalytic amount of [1,1'-di-methyl-3,3'-methylenediimidazoline-2,2'diylidene]$PdBr_2$, led to the formation of trifluoroacetic acid methyl ester.

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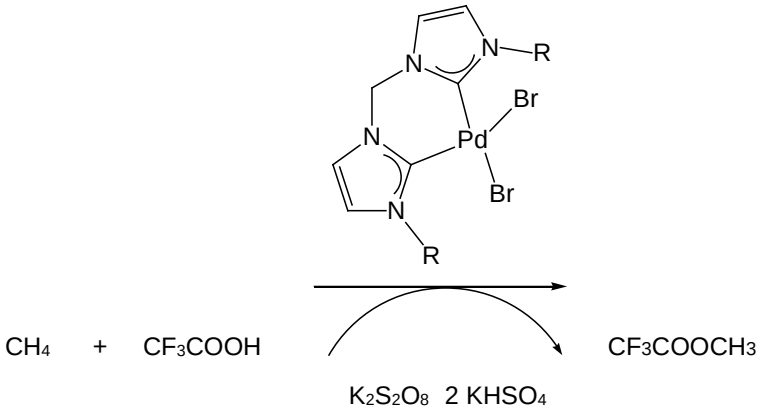

Figure 4. Palladium N-heterocyclic carbene catalyzed C–H activation of methane.

Apart from C–C bond forming reactions, palladium N-heterocyclic carbene complexes are also useful catalysts for hydrogenation reactions of olefins at room temperature, which is of great interest since non-catalytic hydrogenation reaction takes place at very high temperatures.[36]

For example, the hydrogenation of cyclooctene to cyclooctane was achieved even at room temperature, in the presence of palladium catalyst, [1,1'-dimethyl-2,2'-*bis*-methyl-3,3'-methylenediimidazol-4,4'-diylidene]Pd$(CH_3CN)_2(BF_4)_2$.

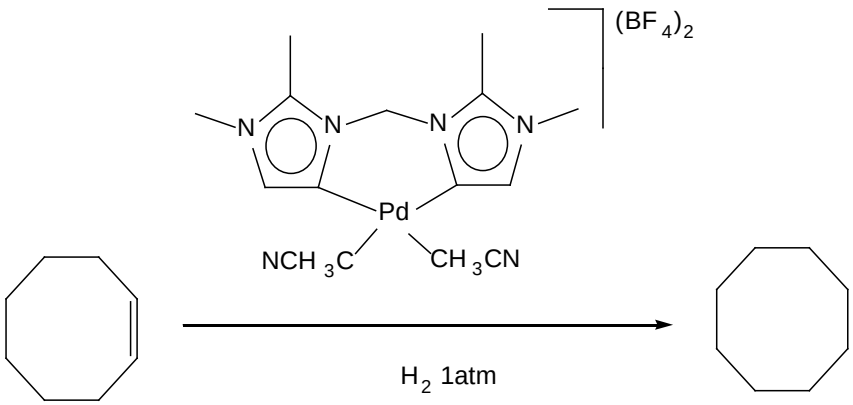

Figure 5. Palladium N-heterocyclic carbene catalyzed hydrogenation reaction of olefin.

III. RUTHENIUM N-HETEROCYCLIC CARBENE COMPLEXES

Several ruthenium N-heterocyclic carbene complexes have been extensively studied in a variety of chemical transformations such as transfer hydrogenation,[37] C–H activation,[38] cycloaddtion,[39] isomerization,[40] olefin metathesis,[41] alkene–alkyne coupling reaction,[42] hydrosilylation reaction[43] and other catalytic processes.[44]

In the case of transfer hydrogen reaction, that provide an alternative of conventional hydrogenation reaction, the reaction involves the transfer of hydrogen from a donor to an unsaturated compound occurs to yield the reduced product.

The transfer hydrogen reaction offers simple, safe and low cost strategy to create new stereocenters, primarily from the reduction of ketones and aldehydes.[45] For example, in a transfer hydrogen reaction, acteophenone was converted cleanly to 1-phenylethanol in presence of [1-(4,4-dimethyl-4,5-dihydrooxazol2-yl)-(3-mesityl)imidazo-2ylidene]RuCl(*p*-cymene)(PF_6) catalyst.

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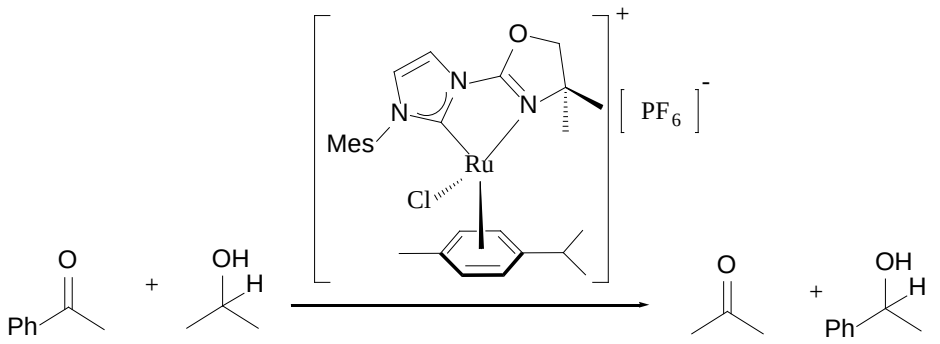

Figure 6. Ruthenium N-heterocyclic carbene catalyzed transfer hydrogenation reaction.

Olefin metathesis, a carbon–carbon double bond rearrangement methodology, leads to the formation of many fine chemicals, natural product and polymers compounds, and which are conveniently achieved by a ruthenium N-heterocyclic carbene based olefin metathesis catalysts, also better known as the Grubs' 2nd generation catalyst.[46] The reaction of but-2-ene and 1,2-dipenylethene gave the cross-metathesis product 1(prop-1-enyl)benzene in presence of the [1,3-*bis*-(2,4,6 trimethylphenyl)imidazolin-2ylidene](PPh$_3$)Cl$_2$Ru=CHPh catalyst.

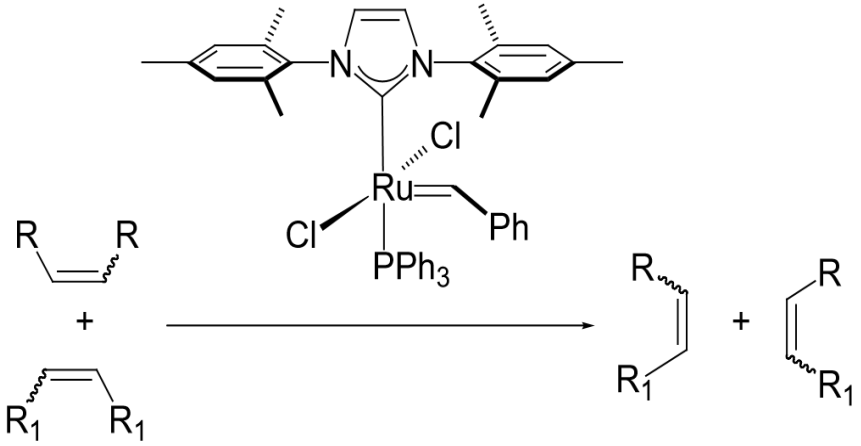

Figure 7. Ruthenium N-heterocyclic carbene catalyzed metathesis reaction.

Radical polymerization is a versatile method for obtaining polymers with controlled molecular weight and molecular weight distributions for a wide of monomer substrates. Kharasch addition,[47] a special case of radical polymerization, where the olefin is used in stoichiometric amount with respect to the halogen compound is successfully catalyzed by the ruthenium N-heterocyclic carbene complexes. For example, when CCl_4 was added in stoichiometric amount to styrene, in presence of the ruthenium catalyst, [1,3-*bis*-(2,4,6 trimethylphenyl)(4,5-di-methyl)-imidazolin-2-ylidene]Ru(*p*-cymene)Cl_2, the formation of 1-(1,3,3,3,-tetracholorpropyl)benzene was observed.

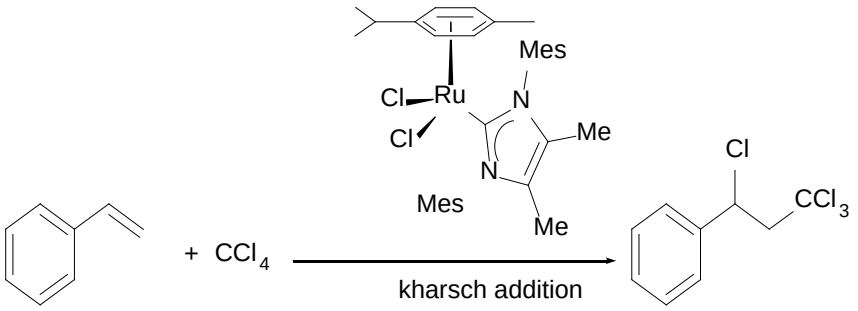

Figure 8. Ruthenium N-heterocyclic carbene catalyzed Kharsch addition.

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The ruthenium N-heterocyclic carbene complexes have been successfully utilized in reduction of nitrile group to give amine functionalized compounds that are of biological importance.[48]

For example, reduction of benzonitrile to benzyl amine was achieved under ligand assisted catalysis conditions, where the active catalyst was generated *in-situ* by the reaction of 1,3-*bis*-(2,4,6 trimethylphenyl)-imidazolium bromide salt with [Ru(cod)methylallyl$_2$].

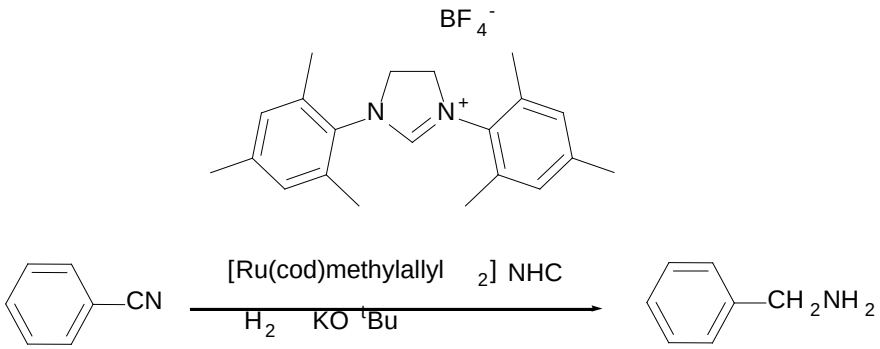

Figure 9. Ruthenium N-heterocyclic carbene catalyzed reduction of benzonitrile.

Recently, ruthenium N-heterocyclic carbene complexes have been employed for the oligomerization of terminal alkynes to obtain valuable materials with applications in electronic, liquid crystalline, optical and magnetic devices.[49]

Specifically, the ruthenium catalyst, [(1-butyl-3-methylimidazol-2-ylidene)]RuCl$_2$(*p*-cymene), was successfully tested for oligomerization of phenylacetylene giving polyphenylacetylene polymer.

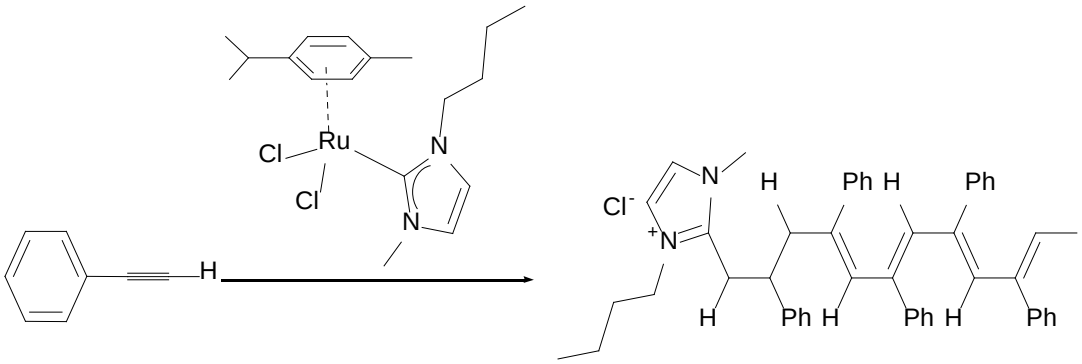

Figure 10. Ruthenium N-heterocyclic carbene catalyzed oligomerization of terminal alkyne.

IV. CONCLUSION

In summary, the importance of the transition 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 Pd and Ru complexes of N-heterocyclic carbene in homogenous catalysis.

Designing and developing better catalyst is a constant ongoing challenge 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.

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