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Schiff base metal complexes of Ni, Pd and Cu

Oshin Sebastian and Ashwin Thapa

Department of Chemical Engineering, SRM University, Kattankulathur, Chennai

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ABSTRACT

In this review paper we talk about the Schiff base ligands and its complexes with metals. In the past few decade there have been an increased interest in this area. . Synthesis of Schiff base can be done in many ways in which most common is the nucleophilic attack of amines on the electrophilic carbon of aldehydes or ketones. The end result of this reaction is a compound in which C=O double bond is replaced by a C=N double bond. Schiff base complex formation with transition metals are easier because of the incomplete d or f shells. Schiff base metal complexes are widely studied because of their industrial, antifungal, antibacterial, anticancer and herbicidal applications. The Suzuki-Miyaura or Suzuki reaction is one of the most important reactions in organic chemistry as it is an extremely powerful reaction for carbon-carbon bond formation and yet rather easy to carry out. The Suzuki-Miyaura coupling reaction has enabled the syntheses of many compounds on an industrial scale due to its cost-efficiency. Schiff base derived transition metal complexes have been identified as effective catalyst for Suzuki-Miyaura reaction. Later on different complexes of transition metal such as Palladium, Copper and Nickel are discussed. Each complexes depending up on the ligand used showed different properties such as antimicrobial, antifungal, antibacterial, antioxidant etc. Catalytic activities of Nickel and Palladium metal complexes and application of these complexes also discussed

Keywords: Schiff base, coordination chemistry, Metal complexes, Transition metals, catalyst, Suzuki-Miyaura reaction, Palladium complex, Nickel complex, copper complex

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INTRODUCTION

In the past two decades, the field of catalysts has seen a boom with numerous groups successfully developing newer and better complexes – each complex having higher efficiency or lower loading ratios or lower toxicity, etc. Transition metal complexes based on Schiff base ligands have received a bigger proportion of attention due to their diverse structural features. Transition metals are metallic elements that have an incomplete d or f shells in the neutral or cationic states. These incomplete valance shell orbitals allow it to accept electrons from Lewis bases to form coordination complexes very easily compared to other group of elements. Ligands therefore must be a Lewis base. They must contain at least one pair of non-bonding electrons that can be donated to a metal ion. This is when Schiff base ligands come into the picture.

A Schiff base is a compound with functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$, where R is an organic side chain. It is usually formed by the condensation of an aldehyde or ketone with a primary amine. Schiff bases have also been shown to exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Imine or azomethine groups are present in various natural, naturally derived, and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities. Schiff bases are important compounds owing to their wide range of industrial applications.

Transition metal complexes based on Schiff base ligands are very efficient catalysts in both heterogeneous and homogeneous reactions. The activities of these complexes vary depending on the coordination sites, ligands and central metal ions. Analysis of catalytic activity of transition metal complexes in various reactions are done and found that the catalytic activity of transition metal Schiff base complexes shows variations with structure and type of Schiff base ligands present [1].The easy electron donating ability of Schiff base ligands plays an important role in carrying out reactions at low temperatures. These experiments have showed that these complexes are of commercial importance and highly useful in industries. Hassan et al synthesised new symmetrical [N4O2] hexadentate Schiff base ligand, and its complexes of Ni (II), Cu (II), Zn (II), Co (II), Cd (II) and Mn (II). These complexes are characterised by different physio-chemical techniques and activity data shows these synthesised complexes have more potent antibacterial activities than parent Schiff bases. Likewise there are many groups who have been successful in developing new Schiff base transition metal complexes which have high biological activity. These studies show that these complexes have the ability to influence the yield and selectivity of chemical reactions. Thus it's necessary to analyse these complex formation of Schiff base with different transition metals and to identify their biological importance and applications.

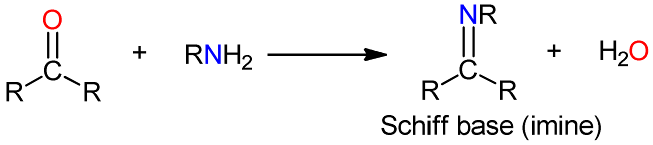
Schiff Base

Hugo Schiff (Scheme 1), one of the founders of modern chemistry, discovered the Schiff base. The Schiff base is named after Hugo Schiff and is a compound with a functional group that contains a C-N double bond with the nitrogen connected to an aryl or alkyl group. Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$, where R is an organic side chain. Schiff base is synonymous with azomethine and may also be referred to as imines.

Scheme 1: Hugo Schiff (1834-1915)

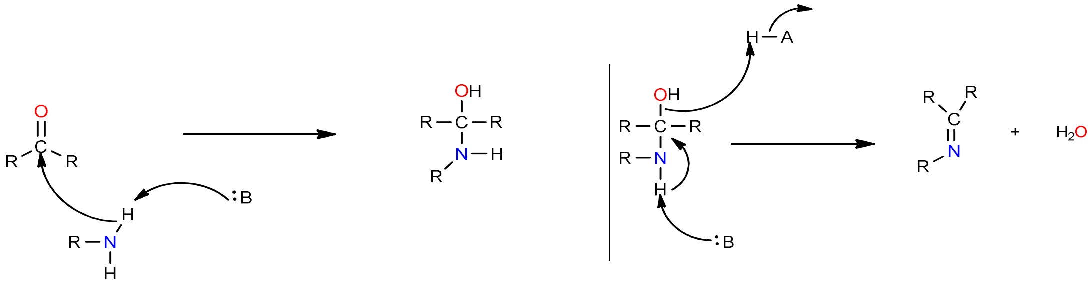
Synthesis of Schiff base

A common method of synthesis of Schiff base is the nucleophilic attack of amines on electrophilic carbon of aldehydes or ketones. The end result of this reaction is a compound in which C=O double bond is replaced by a C=N double bond (Scheme 2).This type of compound is called an imine or a Schiff base.



Scheme 2: Synthesis of Schiff base

The mechanism of Schiff base formation involves two major steps (Scheme 3). First is the attack of the amine nitrogen on the carbonyl carbon. The nitrogen is deprotonated and the electrons from this N-H bond then push the oxygen off the carbon, forming a C=N double bond and displaced water molecules. We can convert the imine back to aldehyde or ketone by simple hydrolysis.



Scheme 3: Mechanism of Schiff Base formation

Other methods of preparation of Schiff base are by Oxidative synthesis of imines from alcohols and amines, oxidative synthesis of imines from amines, addition of organometallic reagents to cyanides, reaction of phenols and phenol-ethers with nitriles, oxidation of metal amines to imines by 2-bromoanisole and Conversion of α-amino acids into imines [4].

Complex formation of Schiff base

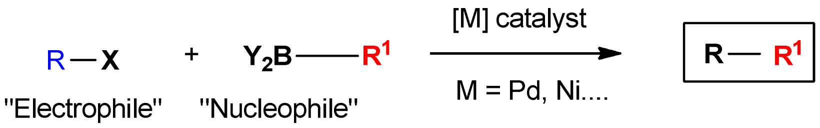
Schiff base have been used as chelating ligands in coordination chemistry and metal complexes of these ligands attracted great interest. Schiff base metal complexes are widely studied because of their industrial, antifungal, antibacterial, anticancer and herbicidal applications. Chelating ligands containing N, O and O donor atoms show broad biological activity. These are of special interest because of the special way they are bonded to the metal ions. It is also known to us that metal ions bonded to biologically active compounds may enhance their activities. There is an infinite number of possible Schiff base metal complexes with a multitude of ligands available compounded with different coordination environments. Studies reveal that Schiff bases possess an innately strong ability to form complexes [5].

Metal complexes of Schiff base find applications in various fields: the most prominent is in the field of catalysis. Aromatic Schiff base or their metal complexes catalyse reactions on oxygenation, hydrolysis, electro-reduction and decomposition. Copper complexes, derived from amino acids enhance the rate of hydrolysis by 10-15 times as compared to simple copper (II) ions. Synthetic Iron (II) Schiff base complex exhibits catalytic activity towards electro-reduction of oxygen while other metal complexes of a polymer bound Schiff base show catalytic activity on decomposition of hydrogen peroxide. As mentioned earlier, these complexes have strong biological activities. Many tridentate Schiff bases and Schiff bases derived from furylglyoxal and p-toluidene show antibacterial activity in E.coli, S.aureus, and Bacillus Subtilis and Proteus vulgaris. Chromium azomethine complex, cobalt complex Schiff base, unsymmetrical complex chromium dyes give colour to leathers, food packages, wools etc. very quickly. Azo groups containing metal complexes are used in dying cellulose polyester textiles and cobalt complexes of Schiff base have excellent light resistance and do not degrade in acidic gases. Several Schiff bases possess anti-inflammatory, analgesic and anti-oxidative action [6]

Suzuki-Miyaura Coupling Reaction

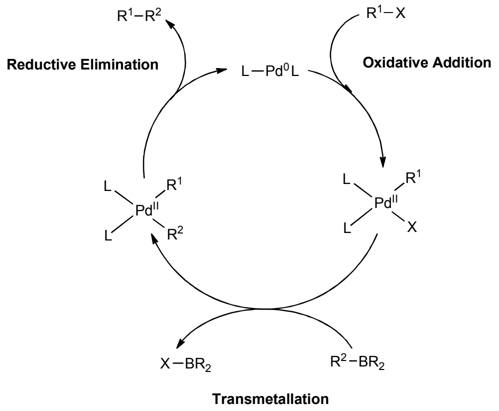
The Suzuki-Miyaura or Suzuki reaction is one of the most important reactions in organic chemistry as it is an extremely powerful reaction for carbon-carbon bond formation and yet rather easy to carry out. This reaction opened a pathway to a vast number of compounds previously inaccessible owing to the difficulties of producing those compounds. Today, there are thousands of catalysts that can effectively promote this reaction. In which most important is Schiff base derived transition metal complexes. These complexes serve as the best catalyst under mild conditions.

The reaction involves a reaction between an electrophilic halide and a nucleophilic organo-boron derivative in the presence of a palladium catalyst and a base (Scheme 4).



Scheme 4: Suzuki-Miyaura Reaction

Palladium first reacts with the electrophile and undergoes oxidative addition to form an organopalladium complex that contains the alkyl group now. This compound on transmetallation with the nucleophile yields another organopalladium complex which on reductive elimination yields the palladium metal again and the desired product R1-R2 (Scheme 5)



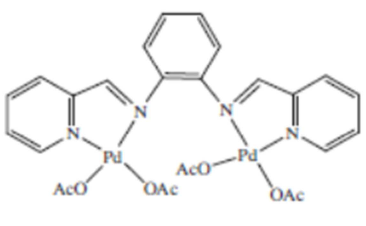
Scheme 5: Mechanism of Suzuki-Miyaura reaction

The Suzuki-Miyaura coupling reaction has enabled the syntheses of many compounds on an industrial scale due to its cost-efficiency. The reasons for its cost-efficiency is due to organo-boron compounds being relatively cheap and easy to produce, catalyst loading being heavily minimised and the conditions required for the reaction being vastly milder than before the reaction was discovered. The Suzuki reaction is also relatively environmentally-friendly; water can be used as a solvent which includes all water-soluble compounds into the possibilities of nucleophiles. This reaction is continuously being improved upon over the years and many substitutes for the organoboron compounds have been discovered such as organotrifluoroborate salts and boronic esters. Also, the latest metal complex with a phosphine ligand has been reported to have a catalyst loading significantly smaller than complexes used in the past. The sheer number of possibilities and combination of types of ligands, coordination, type of metal complex catalyst, types of nucleophiles and electrophiles speak for the immense utility of this reaction. The Suzuki reaction finds applications in pharmaceuticals, medicine and in the production of complex compounds.

Schiff base derived metal complexes

Palladium is a versatile metal for catalysis. Over the past few years there has been a considerable amount of interest in developing new phosphorous-free palladium catalyst with high stability and activity that would also allow reaction to proceed under moderate conditions. In this section, we will review some important complexes synthesised in past years and their importance and applications.

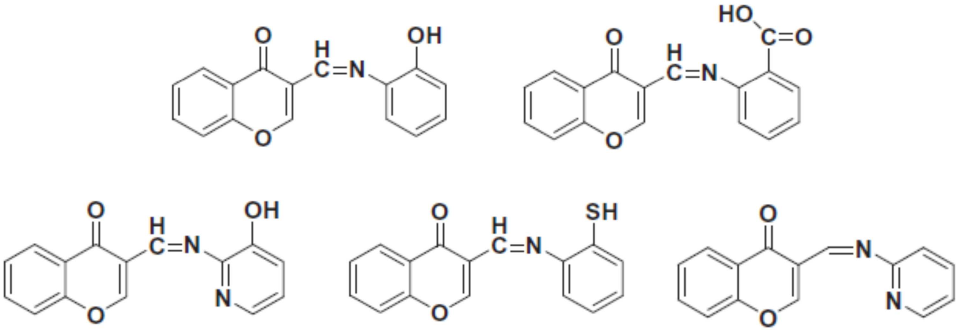
The problem in Suzuki Miyaura reaction is the high catalyst loading. There has been much effort from all around the world in tackling this problem. A new palladium Schiff base catalyst were developed which showed excellent catalytic activity in Suzuki Miyaura reaction of aryl chlorides with low catalytic loading (0.2%) [7]. Previously reported ligand N,N'-bis(benzylidine)-o-phenylenediamine (L) (Scheme 6) were made to react with $PdCl_2$ in acetonitrile to obtain complex 2 (Scheme 7). Efficiency of this complex as catalyst for the Suzuki–Miyaura reaction were studied for the reaction between 4-chloronitrobenzene and phenylboronic acid. Initial reaction was conducted at room temperature using DMF as solvent and K_2CO_3 as base with 1.0 mol %of the catalyst. Best result was obtained at 100 ^oC with in 1 hour of reaction time (98% yield). It is well established that in the Suzuki reaction the choice of solvent, temperature and concentration of complex catalyst plays a crucial role in the overall performance of a catalyst. To investigate this reactions are carried out in different solvents, temperature and different catalyst concentration. Optimized condition was found to be (DMF, K_2CO_3, 100 ^oC, 0.2 mol % complex 2)



Scheme 6: N,N'-bis(benzylidine)-o-phenylenediamine (L)

Scheme 7: complex formation of Ligand L in the presence of PdCl2 and Acetonitrile

Other groups [8] have successfully synthesized Pd(II) complexes of 3-formyl chromone Schiff bases such as HL1, HL2, HL3, HL4 and L5.(scheme 8 and table 2). Palladium complexes with theses ligands showed good antimicrobial activity and two Gram (-ve), two Gram (+ve) and fungal microorganisms and the results indicate that, complexes show better microbial inhibition activity than the ligands. Also Palladium complex of HL1 ligand have shown potential as an antioxidant.

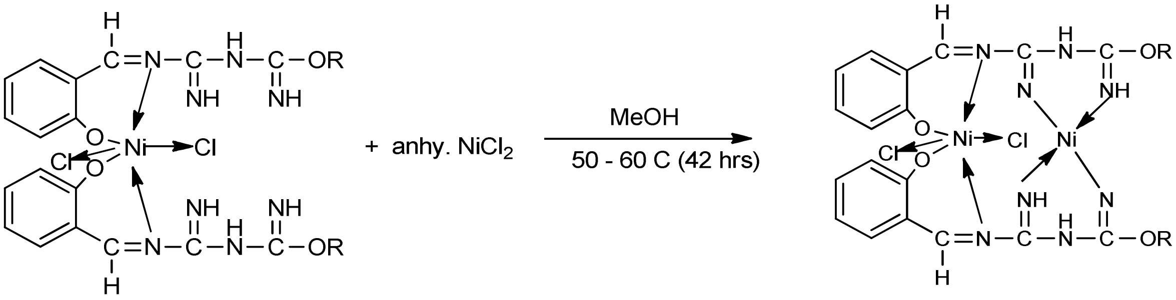


Scheme 8: Clockwise from left hand top HL1, HL2, HL3, HL4 and L5

HL1	3-(-(2-hydroxyphenylimino)methyl)-4*H*-chromen-4-one
HL2	2-((4-oxo-4*H*-chromen-3-yl)methyleneamino)benzoic acid
HL3	3-((3-hydroxypyridin-2-ylimino)methyl)-4*H*-chromen-4-one
HL4	3-(-(2-mercaptophenylimino)methyl)-4*H*-chromen-4-one
L5	3-((pyridin-2-ylimino)methyl)-4*H*-chromen-4-one

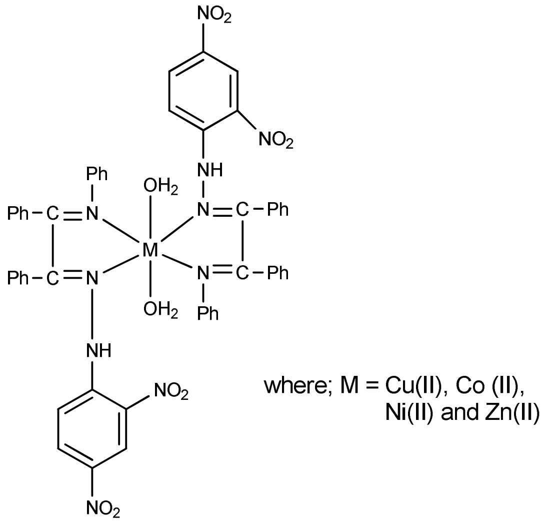
Table 1

On the other hand, Nickel, another transition group element also shows high activity towards complex formation with Schiff base compounds. Nickel complexes with multidentate Schiff base ligands have the ability to exhibit different oxidation states in their complexes. Due to this reason, they play an important role in bio-inorganic chemistry. These complexes are mainly used as catalyst in industries. Nickel (II) complexes with tetra-dentate N_2O_2 Schiff base ligands derived from salicylaldehyde act as a hydrogenation catalyst of zeolites [9]. Nickel (II) complexes with Schiff base ligands are derived from the condensation of bis (1-amidino-O-methylurea) Ni (II) chloride and salicylaldehyde (Scheme 9). Using analytical techniques, the magnetic moment and electronic spectra suggested an octahedral structure [10].



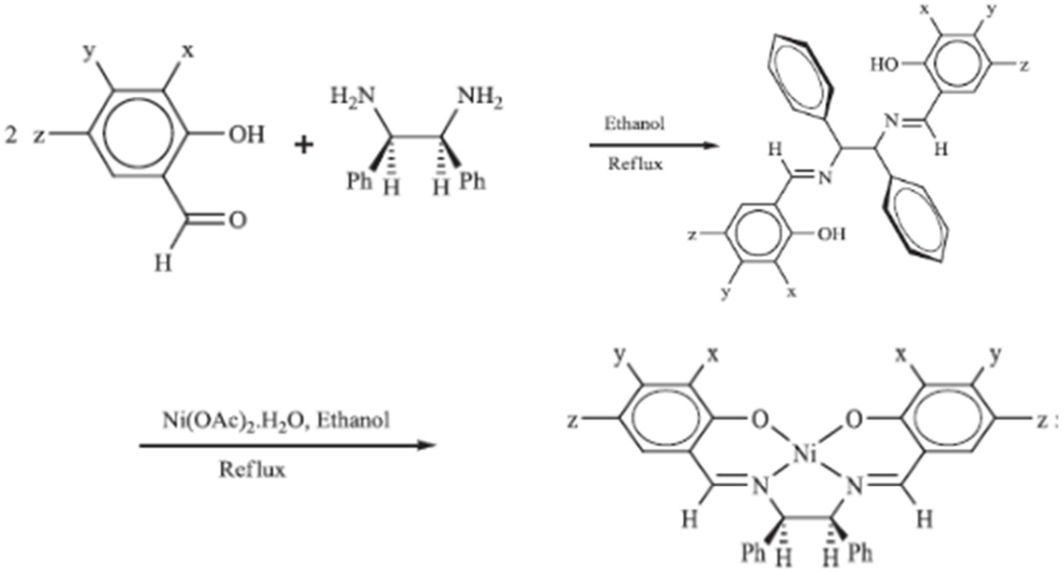
Scheme 9: Synthesis of Nickel (II) complex

A variety of Schiff base can be synthesised by condensation of Benzil-2,4-dinitrophenylhydrazone and aniline. Resulted Schiff base is reacted with Nickel (II) chloride to obtain a Nickel Schiff base complex [11]. After careful investigation of these complex using IR, H NMR, C NMR, UV-Vis, CV and EPR, its structure is revealed and it was found that the ligand binds through its azomethine nitrogen to the metal ion and acts as a bidentate ligand and thus exhibits octahedral geometry. The ligand L, on interaction with Cu(II), Co(II), Ni(II) and Zn(II) chlorides, yields complexes corresponding to the general formula [ML2$(H_2O)_2$]. Structure of the complex is shown below (scheme 10)



Scheme 10: Proposed structure of the complex

As said earlier Schiff base complexes have been used as catalyst in different industrially and laboratory important reactions such as oxidation, reduction and polymerization. Epoxidation of olefins is among the most important reactions in inorganic chemistry because it provides an effective way to produce several invaluable new compounds. Various metal complexes of salen type Schiff base ligands have studied in such reactions. Nickell (II) complexes have also been used as catalyst for epoxidation of olefins. Salen type Schiff base complexes of Ni(II). The ligands were synthesized from the condensation of meso-1,2-diphenyl-1,2-ethylenediamine with n-methoxysalicylaldehyde (n = 3, 4 and 5) (Scheme 11 and table 2). Crystal structure of these complexes are discussed later on in this review paper. Depending up on the value of “n” in n-methoxysalicylaldehyde three different ligands are synthesised (H_2L^1, H_2L^2, H_2L^3). This ligand in the presence of $Ni(OAc)_2.4H_2O$ produced Nickel complexes NiL^1 , NiL^2 and NiL^3 [16].



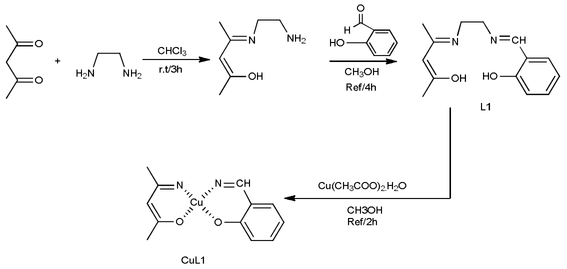
Scheme 11: Synthesis of Salen Schiff base ligand

Ligand and Complex	X	Y	Z
H_2L^1	H	H	H
H_2L^2	H	OCH_3	OCH_3
H_2L^3	H	H	H

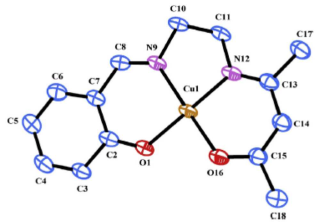
Table 2

Schiff base and their copper complexes also have good applications. They are used in catalysis in biological systems and exhibits antimicrobial activities and antifungal activities. Several models including bi, tri, tetra and multidentate Schiff base ligands and their coordination chemistry of copper attracts much attention because of their biological relevance and also due to its structure and oxidation states. The complexes of copper with Schiff base have wide application in food industry, dye industry, analytical chemistry, catalysis and many other fields. Copper (II) complexes show distorted octahedral and tetrahedral symmetries due to d^9 configuration. This phenomena is called Jahn-Teller effect. The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. Due to this effect Copper (II) complexes have square planar or square pyramidal geometries [12].

A new copper (II) Schiff base complex containing asymmetrical tetradentate N_2O_2 Schiff base ligand was prepared from asymmetrical Schiff base ligand salicylidene imino-ethylimino-pentan-2-one (L^1) and $Cu(OAC)_2$ [13]. The method of synthesis of ligand and its copper (II) complex is shown below (Scheme 12). The complex have been characterized by elemental analysis FT-IR and H NMR. The molecular and crystal structures were determined by single crystal X-ray diffraction. An ORTEP view of the complex is given in Scheme 13. The Schiff base ligand of L1 acts as a chelating ligand and coordinates via two nitrogen and two oxygen atoms to the copper (II) ion with C1 symmetry. The structure of the CuL1 complex was also studied theoretically at different levels of DFT and basis sets.



Scheme 12: synthesis of ligand (L1) and its copper (II) complex (CuL1)



Scheme 13: An ORTEP view of CuL1

Major applications of copper (II) complexes lie in catalytic chemistry. In the recent past, there has been growing interests in the preparation of various copper catalyst and their applications in oxidation of various organic compounds. Since the new trend is to develop greener processes at the same economically viable, polymer supported catalysis in oxidation reactions have been in the spotlight. The activity of polymer supported Schiff base complexes of transition metal ion varies with the type of Schiff base ligands, coordination sites and metal formation. The Schiff base ligand 4-acetylpyridine thiosemicarbazone was used to prepare the polymer supported Cu (II) Schiff base Catalyst [Cu(L)(Cl)2]. The Schiff base ligand and copper (II) were found to exhibit very good activity against Gram +ve and Gram –ve. Developed copper (II) catalyst showed high catalytic activities in oxidation of alkene, alkane and aromatic alcohol. This finding also proved that this polymer supported Cu (II) Schiff base complex catalyst as a useful catalyst to synthesize industrially important organic compounds [14].

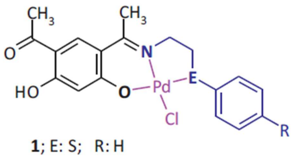
Parallely, other teams synthesized two new pyrazolone based Schiff base ligands 4-((2,4-dimethylphenylimino) methyl)-4,5-dihydro-3-methyl-1-p-tolyl-1H-pyrazol-5-ol [PTPMP-ME] and 4-((3,4-difluorophenylimino)methyl)-4,5-dihydro-3-methyl-1-p-tolyl-1H-pyrazol-5-ol [PTPMP-F] were synthesized. Using these Schiff base ligands two new Copper (II) complexes, [Cu (PTPMP-ME)2] (1) and [Cu(PTPMP-F)2] (2) were also synthesized. Crystal structure data revealed that the two N, O-chelating Schiff base ligands were coordinated to the copper metal centre to create a square planar geometry. Thus, both the ligands form a six membered chelate ring with the copper metal centre. Antibacterial activity data of the ligands and complexes proves that complexes have more activity that their parent ligands. It might be due to the complexation between the ligands and the metal ion [15].

Likewise there are many complex formations with copper that can be used as a potential biological agent. Further investigation is needed to explore such ligands and metal complexes of copper which will be useful in industrial and pharmaceutical purpose. Above mentioned transition metals and complexes is just an example of potential member of coordination chemistry. Transition metal complexes of Schiff base ligands with metals such as Fe(II), Co(II), Zn(II), Cd(II) and many others are also widely investigated. Based on the ligands used and metal ion present, variation in crystal structure arises and coordination sites and hence different biological activities are observed.

Catalytic activity of Palladium and Nickel Schiff base complexes

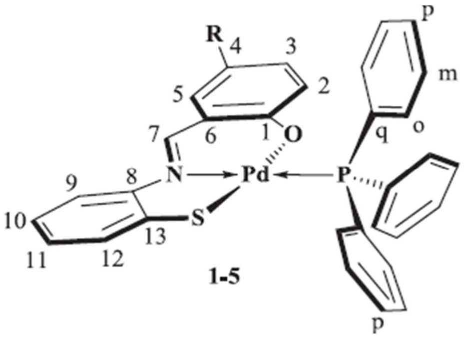
Schiff base ligands are easily synthesised and form complexes with almost every metal ions. Their application in both homogeneous and heterogeneous catalysis are significant. Hence there is a need to review the catalytic activity of Schiff base complexes.

Palladium is a versatile metal for homogeneous and heterogeneous catalysis. A large number of carbon-carbon bond forming reactions such as the Heck and Suzuki coupling are facilitated by catalysis with palladium compounds. During the past 10 years, there has been considerable interest in the development of new phosphorus free palladium catalysts for higher activity, stability and substrate tolerance that allow reactions to be carried out under milder reaction conditions. Palladium (II) complexes with bisimine ligands (scheme 14) as listed below were tested as catalysts in the Suzuki-Miyaura coupling reaction of phenyl boronic acid and aryl and hetero-aryl halides under identical conditions. The catalysts were stable in air at 100°C and no palladium black was observed. Their catalytic activity depended on the aryl halide. It was found that the presence of selenium in complex 3 promoted catalytic activity while the tellurium in complex 5 drastically reduced it. Also, complex 3 was able to yield 20% in the coupling of a few aryl chlorides whereas complex 1 and 5 were completely inactive. [17]



1; E: S; R: H
3; E: Se; R: H
5; E: Te; R: OMe

Scheme 14: Pd (II) complex with Bisimine Ligand

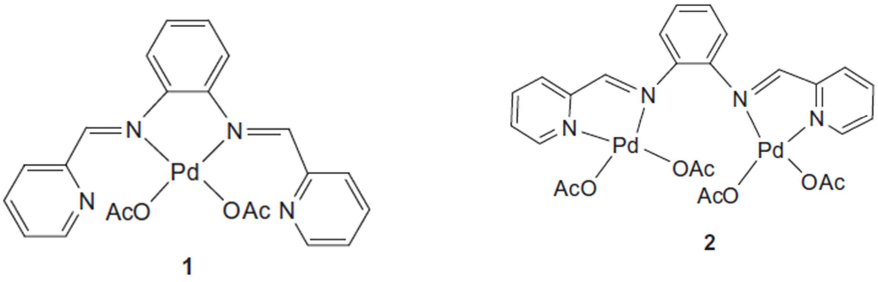


Scheme 15: Pd (II) complexes [R=H (1), CH_3 (2), OCH_3 (3), Cl (4) or Br (5)]

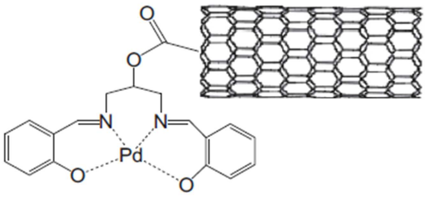
Palladium (II) complexes (complex 3) with salicylideneimine and triphenylphosphine ligands (Scheme 15) were tested with the Suzuki-Miyaura coupling reaction of various aryl bromides and aryl boronic acids. It was found that electron deficient aryl bromides produced excellent yield while aryl bromides with electron-donating groups showed good yield but not as high. 3,5-dimethyl-1-bromobenzene even had a low yield of 65% which has been attributed to the steric effect. Complex 3 also did not produce good yield with heterocyclic aryl halides which has been attributed to the chelating ability of isonicoteine with the metal. The complex is air, light and moisture stable but after catalysing a reaction, palladium black forms. [20]

Complexes 1 and 2 are palladium (II) complexes with N4 Schiff base ligands (Scheme 16). They are stable in air. Their catalytic activity was tested for the Suzuki coupling reaction of arylboronic acid and various aryl halides. The reactions were conducted in water. Complex 2 yielded excellent yield while complex 1 was not efficacious with very low yields. The yield for complex 1 was increased by using a PrOH as base and a 65% yield was obtained. Glucose as a co-solvent with water at a higher temperature produced a large yield. It was also found that the complexes are steric tolerant and produced great yield. [21]

Scheme 16: Pd (II) complexes with N4 Schiff base ligands

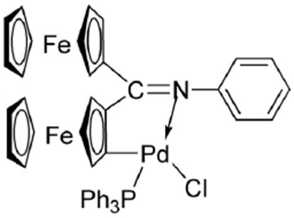


In a little more on the novel side, the catalytic activity of the palladium-Schiff base complex with a multi-walled carbon nanotube shown in Scheme 17, was tested in Suzuki-Miyaura reactions between various aryl halides and benzeneboronic acid. The reaction produced yield all above 90% for para located electron-withdrawing groups and much lower yield for ortho located groups. The reusability of this heterogeneous catalyst was also tested and found that even after a fourth run, the reaction produced 82% yield. [19]



Scheme 17: Palladium-Schiff base complex with a multi-walled carbon nanotube

Also novel, the catalytic activity of a new diferrocenylimine cyclopalladated complex shown above was tested with the Suzuki-Miyaura coupling reaction of iodobenzene and phenyl boronic acid by a group. This reaction obtained a 93% yield and further research on the Suzuki coupling reaction is ongoing. [18]



Scheme 18: new diferrocenylimine cyclopalladated complex

Nickel catalyst are of great interest due to the fact that it's cheap. Different nickel (II) complexes has been synthesised over the past few decades which had high efficiency and selectivity. Nickel complexes has been identified as most the effective catalyst in oxidation of alcohols into carbonyl compounds, which is one of the most pivotal functional group transformations in organic synthesis [22]. A series of nickel (II)-triphenylphosphine complexes with derivatives of N-(2-pyridyl)-N'-(salicylidene) hydrazine has been synthesised (NiL1-NiL5) and their application in oxidation of alcohols to carbonyl compounds in ethyl-methyl imidazolium (EMIM) ionic liquid has been investigated. To study the catalytic activity a solution of nickel complex (0.02 mmol) in 0.1 mL EMIM was added to the solution of benzyl alcohol (1 mmol) and NaOCl (1 mmol) and periodically reaction mixture was removed and analysed using Gas chromatography. It has been observed that total reaction time was only 15 min even at room temperature. This proves that Ni (II) complex/EMIM-NaOCl system showed great efficiency. It has also been observed that catalytic activity reduces dramatically with increase in the size of substituents. To find out the effect of concentration of catalyst with respect to substrate, the reaction was carried out in different substrate to catalyst ratio and it has been found that 0.02 mmol of catalyst was sufficient for maximum conversion of benzyl alcohol to corresponding carbonyl group. This observations shows the catalytic activity of Nickel (II) complexes. Same reaction was studied under different substrates and all the alcohols were oxidized from good to excellent conversions without adding any additives. All nickel complexes were found to catalyse the oxidation of alcohols to corresponding carbonyl compounds in a conversion range of 60-96%. Experimental data's are given in table 3 below [22]

Entry	**Amount of NiL1 (mmol)**	**Amount of NaOCl (mmol)**	**Conversion (%)**
1	0	1.0	1.5
2	0.01	1.0	65.2
3	0.02	1.0	90.6
4	0.03	1.0	89.6
5	0.04	1.0	89.4
6	0.05	1.0	89.3
7	0.02	0	2.6
8	0.02	0.5	44.6
9	0.02	1.5	90.6
10	0.02	2.0	90.5

Table 3

Other major application of Metal complexes is in reduction of benzene. The product cyclohexene is used as a raw material for the production of adipic acid and caprolactum, both of them are intermediates used in the production of Nylon 6 and Nylon 66. Various metal based catalyst are extensively used for reduction of benzene in industry. It has been shown that newly synthesised two new complexes, with the chemical formula, $[M^{II}(L)(Cl)(H_2O)_2]\cdot H_2O$, where M = Ni or Ru and L= 3-hydroxyquinoxaline-2 carboxalidene-4-aminoantipyrine, has the potential to behave as an effective catalyst for the reduction of benzene [23].

The catalytic ability of Nickel (II) Schiff base complex towards hydrocarbon oxidation is well known by now. The synthesis and characterization of new Schiff base complexes of Ni (II) (NiL), where H_2L = *N*,*N*'-bis(2-hydroxyphenyl)ethylenediimine) and its ability to catalyse the epoxidation of olefins in presence of NaOCl has been reported [24]. The synthesised C copper/Nickel complexes of 2,3-bis-[(3-ethoxy-2-hydroxybenzylidene)amino]but-2-enedinitrile Schiff base ligand has reported to show in vitro cytotoxic activity against two cancer cell lines (HeLa and MCF-7 cells)and one healthy cell line (HEK293 cell) [25]. Moreover, the synthesized nickel nanoparticles demonstrated remarkable catalytic performance toward hydrogenation of nitrobenzene that producing clean aniline with high selectivity (98%) [25].

CONCLUSION

The discovery of the Suzuki-Miyaura coupling reaction unlocked areas previously not feasible. Since then, there has been lingering industrial and academic interest and countless advancement in metal complex catalysts. Over the years, many transition metals were tested and popular metals were palladium, nickel, copper and cobalt to name a few. Their metal complexes were easy to produce, economically viable and had numerous applications owing to their high catalytic activities, antibacterial and antifungal properties, antitumor, and good biological activities, among others. . However, there are still many untested potential combinations of metals and ligands and challenges that need to be tackled in the future. Attempts at producing a non-toxic catalyst have been made as a catalyst that can be used with water as the base has been produced but with low yield even after long reflux time and relatively high catalyst loading Such challenges call for a need for catalysts' improvements in their activity while reducing catalyst load, reflux time, eliminating the toxicity of industrial metal complex usage, reducing catalyst poisoning, improving catalyst reusability, finding efficient methods of producing difficult complexes that are stable at high temperatures, etc. to widen the scope and the immense utility they already have.

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