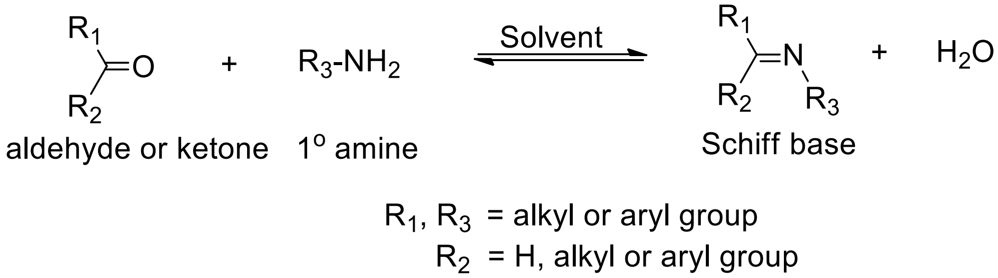
# Chapter 7

# Transition Metal Complexes of Hydrophilic Schiff Bases: A Green Catalysis Approach

**Amlan Puzari**
Department of Chemistry,
Dibrugarh University,
Dibrugarh-786004, Assam, India.
Email: amlanjyotipuzari@gmail.com

## 7.1 Schiff Bases:

Schiff bases are the compounds containing at least an imine (-C=N-) linkage with the N atom(s) directly connected to an aryl or alkyl group [1]. These were first reported by an Italian chemist Hugo Schiff (1834-1915) long back in 1864 which are classically synthesized through condensation of a primary amine and an aldehyde or ketone, although ketones undergo condensation less readily than aldehydes.



**Scheme 7.1.** General synthesis of Schiff bases

The reaction produces water along with the imine product and is reversible in nature. Thereof, the presence of any dehydrating agent likes $MgSO_4$ or zeolites enhance the formation of Schiff bases [2, 3]. Schiff bases are widely studied because of their easy synthetic route, air stability and cost-effectiveness of the precursor materials. These compounds show versatile biological activities such as antibacterial, antioxidant, antiviral, antifungal, antimalarial, antipyretic, antiproliferative, anti-inflammatory etc. [4]. These are also important from industrial perspective as some of these compounds could be employed to prevent various physico-chemical processes like photo-degradation of polymers [5, 6]. Schiff bases also act like ligands to form coordination complexes with metal atoms/ions through the nitrogen atoms. However, some other electronegative atoms such as oxygen, sulphur etc. may also simultaneously coordinate with the metal center resulting in more stable complexes [7].

Since the first report in 1933 [8], variety of such transition metal complexes of Schiff bases have been successfully applied in drug design [9], analytical science and imaging [10, 11], model designing of metalloenzymes [12], metal ion sensing [13] and numerous organic transformations like cross cross-coupling [14-16], hydrogenation [17], oxidation [18] etc. as homogeneous catalyst.

## 7.2 Transition Metal Complexes of Hydrophilic Schiff Bases:

Transition metal complexes of salen-type schiff bases are the most popular and associated with versatile steric, electronic and lipophilic properties for which they have occupied a major domain of schiff base complexes. These types of simple Schiff bases are derived from a diamine and salicylaldehyde derivatives. They have two covalent and two coordination sites to bind with a metal center orientated in planar geometry, with two vacant axial sites around the metal for additional bonding [19].

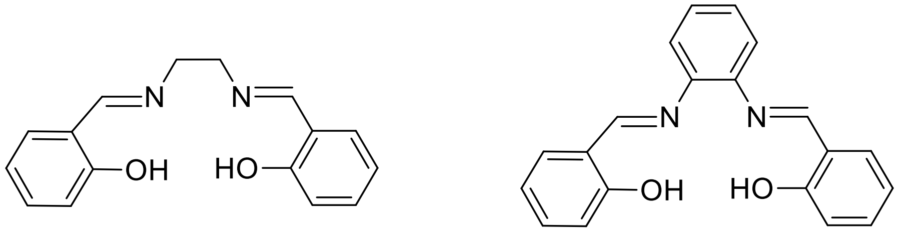


**Figure 7.1.** Salen type Schiff bases

However, numerous non-salen schiff base complexes of various transition metals are also known [4]. Most of the these Schiff base complexes usually get dissolved to form homogeneous solutions in alcoholic media or undesirable, non-green organic solvents like Chloroform, Dimethylformamide (DMF), Dimethylsulfoxide (DMSO) etc.

Therefore, those complexes show active catalytic performance in non-aqueous, organic reaction media [15]. But during the recent decades, use of water in the laboratories as well as industrial sectors has become enormously popular as it offers an inexpensive, readily available and environmentally benign alternative to the conventional hazardous organic solvents. Moreover in an organic synthesis, the product can be separated from the reaction mixture by simple biphasic extraction when water is used as the reaction media [21]. But, a transition metal complex could be effective in accelerating an organic reaction if it gets dissolved completely in the reaction media. Unfortunately, majority of the earlier reports deal with Schiff base complexes which are insoluble in water. From the last few decades thereof, challenges emerged out for the scientific community to design schiff bases and their metal complexes with inherent hydrophilic property. Consequently, an extended series of water soluble schiff base complexes have been synthesized to evaluate their catalytic, pharmaceutical as well as biological activities in aqueous media. Such hydrophilic Schiff base complexes have been employed in many industrially important reactions like coupling [22], oxidations [23, 24], reductions [25] etc. It has been formulated by many experimental researchers that the steric, electronic and some other physical properties, viz. solubility of the Schiff bases could be fine-tuned by choosing the appropriate condensing partners carefully or by introducing some characteristic functionalities to the precursor aldehydes [26].

Likewise, hydrophilicity in the these complexes could be achieved simply by adding some ionic substituents viz. $-SO_3Na$, -COONa etc. to the ligand system that helps in executing their catalytic and biological activities in aqueous media [21].

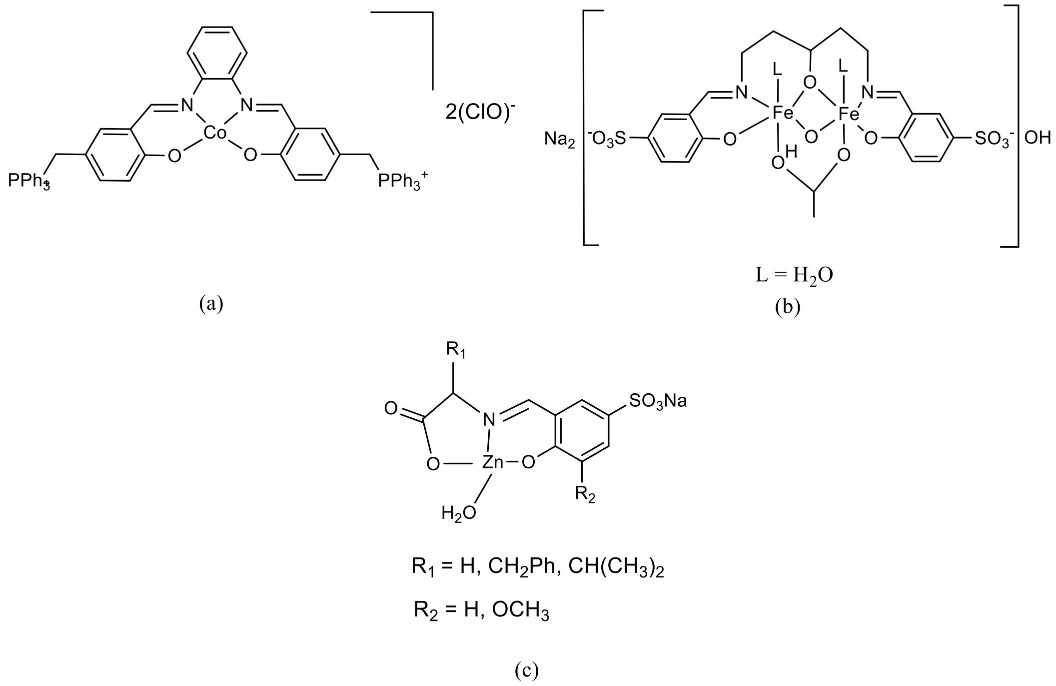


**Figure 7.2.** Water soluble Schiff base complexes [27-28, 34]

## 7.3 Hydrophilic Transition Metal-Schiff Bases Complexes in Green Catalysis:

Transition metal complexes of Schiff bases play a key role in various homogeneous catalytic reactions. Literature reveals that hundreds of such complexes comprising of different types of Schiff bases have been synthesized since the beginning and employed them in catalysis. But after the development of the Green Chemistry concept, use of water as the reaction media for synthesis of organic compounds in laboratory as well in industries using a suitable catalyst has drawn tremendous importance. Likewise, designing of catalyst functional in pure aqueous media has been an emerging trend during the recent decades and consequently from different parts of the globe, many researchers have put their continuous efforts to synthesize water soluble Schiff base complexes of transition elements [27-29]. In fact, there are several such reports on water soluble i.e., hydrophilic Schiff base complexes acting as potential catalyst in various organic reactions compatible with conventional catalytic systems. Likewise, Zhou et al. synthesized a series of hydrophilic Schiff bases and their palladium complexes and applied them for activation of a wide range of electronically and sterically challenging aryl bromides as well as chloride towards Suzuki-Miyaura cross-coupling reaction [20] in aqueous media. During the work, the researchers observed that on addition of a phase transfer reagent like TBAB (tetrabutylammoniumbromide), the rate of the reaction got increased. The most striking advantage of the catalyst was that after completion of a single run, the catalyst remained in the aqueous phase on biphasic extraction of the organic product and hence the aqueous part could be reused up to several catalytic cycles [14].

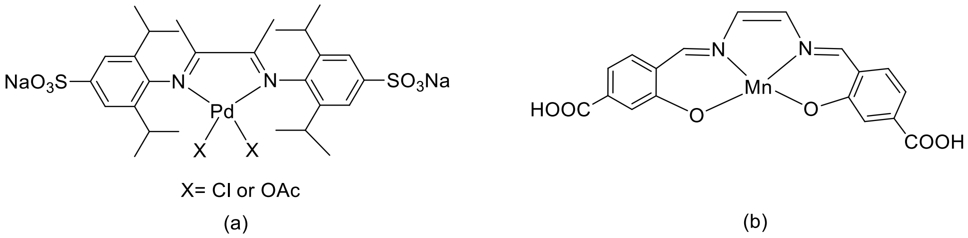
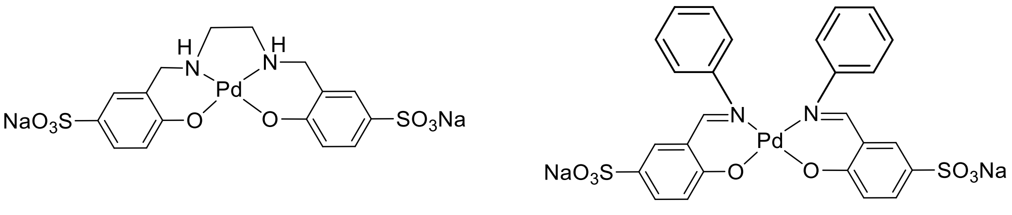


**Figure 7.3**. Hydrophilic Pd-Schiff base complex [20, 23]

Similarly, Liu et al. also synthesized several water-soluble salen coordinated Pd complexes and employed them as active catalysts for Suzuki-Miyaura reactions in pure aqueous media. They reported that the protocol could be highly effective in synthesizing aryl-substituted carbazolyl compounds [15].

Oxidation of sulfides is another important reaction as the sulfoxides and sulfones thus formed as products are typically important for synthetic organic chemistry and toxicological studies. Thus to execute the catalytic potential in oxidation of those compounds, Allard et al. synthesized a water soluble Schiff base complex of Mn (III) containing -COOH groups at the two terminals. Interestingly, the oxidation carried out using $H_2O_2$ in presence of the catalyst was observed to be exclusively chemoselective [23]. However, Schiff bases are sometimes difficult to use as aqueous phase catalyst owing to their propensity to hydrolysis. Under this condition, hydrogenation of the imine C=N bonds takes place forming amines with much better stability. Therefore, Voronova et al. synthesized a water-soluble Pd-tetrahydrosalen complex and applied for hydrogenation and redox isomerization reactions. The complex showed outstanding activity towards these reactions in aqueous media under mild experimental conditions [21].



(a)

(b)

**Figure 7.4.** Pd-tetrahydrosalen and Salen-Pd catalyst [21, 31]

Recently, Shahnaz et al. also synthesized a hydrophilic salen-Pd (II) catalyst for activation of aryl as well as heterocyclic chlorides towards Suzuki-Miyaura cross-coupling reaction under ambient reaction conditions. The homogeneous catalyst could be successfully reused up to several cycles; although a gradual decrease in effectiveness was observed [31]. Apart from simple Schiff base derived complexes, Zhou et al. reported a few water-soluble cyclopalladated Schiff base complexes bearing N-phenylsulfonate groups. They employed the complexes for screening of catalytic activity in Suzuki-Miyaura cross-coupling reactions and observed that one of those hydrophilic complexes was reusable for five consecutive cycles [32].

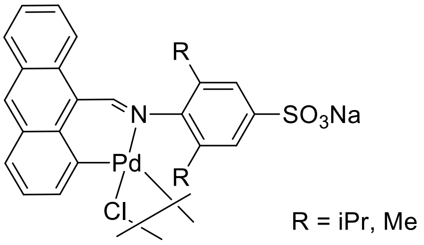


**Figure 7.5.** Water-soluble cyclopalladated Schiff base complex [32]

Binuclear complexes are found to be more effective as catalyst owing to the inherent synergic effect capable of activating two reactant molecules at the same time. Therefore to evaluate the catalytic potential in Suzuki-Miyaura cross-coupling reaction, Hanhan et al. synthesized several binuclear Pd (II) complexes of hydhophilic Schiff bases and observed that they did show excellent rate enhancing potential in aqueous media. The researchers could also recycle the catalysts up to more than ten cycles without any loss in catalytic activity [33].

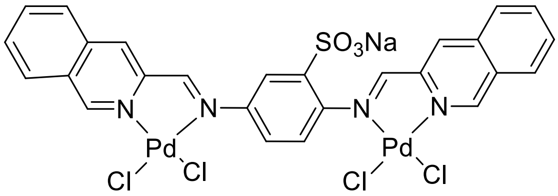


**Figure 7.6.** Binuclear water soluble Pd (II)-Schiff base complex [33]

Similarly, Palopoli and co-workers also synthesized a dinuclear water soluble sulfonated Schiff base complex having Mn (III) as the metal centers. This complex possessed triply bridged diMn (III) core that mimics the coordination geometry of the Mn catalases. It showed excellent catalytic activity towards disproportionation of $H_2O_2$ [30].

The $\eta^6$-arene-Ru (II) complexes are an important class of organometallic compounds exhibiting extensive catalytic properties in a number of organic reactions. Accordingly, Talouki et al. synthesized two water-soluble Ru (II) complexes of Schiff base ligands and employed them as catalysts in aqueous transfer hydrogenation of aldehydes and ketones [17]

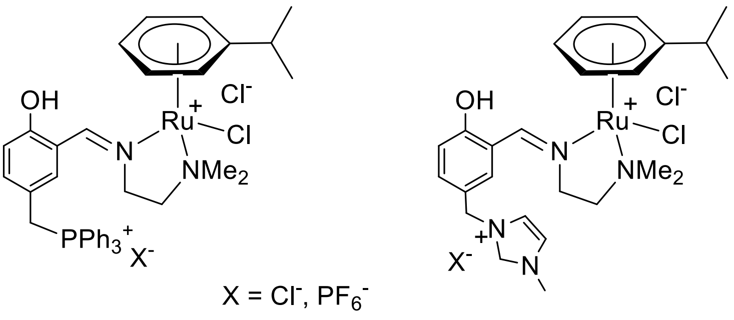


**Figure 7.7.** $\eta^6$ - arene-Ru (II) complexes containing hydrophilic Schiff base moiety [17]

## 7.4 Conclusions and Future Scopes:

In the emerging era of green chemistry all around the globe, development of efficient catalytic systems functional in aqueous reaction media is highly demandable. Therefore in this chapter, advancement in hydrophilic Schiff base chemistry has been discussed from the viewpoint of transition metal directed green catalysis of various industrially important organic transformations. From the literature reports, a number of such water soluble Schiff base complexes of different transition metals with their catalytic potential have been reviewed in detail. Although many hydrophilic complexes have been reported so far with classically varying Schiff bases, chemists are still working for more efficient complexes capable of activating the challenging substrates for a particular organic conversion under ambient experimental conditions so that costly heterogeneous catalysts, conventionally used in popular chemical industries could be replaced in future.

## 7.5 References:

1. O. Sebastian, A. Thapa, J. Chem. Pharm., 7(10) (2015) 953-963

2. P. Das, W. Linert, Coord. Chem. Rev., 311 (2016) 1-23
3. K.C. Gupta, A. K. Sutar, Coord. Chem. Rev., 252 (2008) 1420-1450
4. T. Baran, A. Mentes, H. Arslan, Int. J. Biol. Macromol., 72 (2015) 94-103
5. Z. Hussain, E. Yousif, A. Ahmed, A. Altaie, Org. Med. Chem. Lett., 4(1) (2014)
6. Z. G. Hong, X. M. Zhang, T. X. Wu, C. Zheng, B. Luo, J. Tang, F. P. Huang, D. Yao, H. D. Bian, Polyhedron, 159 (2019) 355-364
7. G. Yadav, J. V. Mani, Int. J. Sci. Res., 4(2) (2015) 121-127
8. P. Pfeiffer, E. Breith, E. Lübbe, T. Tsumaki, Liebigs Ann. chem., 503 (1933) 84-130
9. M. Shabbir, Z. Akhter, I. Ahmad, S. Ahmed, M. Shafiq, B. Mirza, V. McKee, K. S. Munawar, A. R. Ashraf, J. Mol. Struct., 1118 (2016) 250-258
10. P. G. Cozzi, L. S. Dolci, A. Garelli, M. Montalti, L. Prodi, N. Zaccheroni, New J. Chem., 27 (2003) 692-697
11. L. Zhou, P. Cai, Y. Feng, J. Cheng, H. Xiang, J. Liu, D. Wu, X. Zhou, Anal. Chim. Acta, 735, (2012) 96-106
12. E. J. Jarson, V. L. Pecoraro, In Manganese Redox Enzymes, VCH: New York, (1992) 1-28
13. M. Yıldız, N. Demir, H. Unver, N. Sahiner, Sens. and Actuat. B Chem., 252 (2017) 55-61
14. J. Zhou, X. Guo, C. Tu, X. Li, H. Sun, J. Organomet. Chem., 694 (2009) 697-702
15. Y. Liu, N. Gu, P. Liu, X. Ma, Y. Liu, J. Xie, B. Dai, Tetrahedron, 71 (2015) 7985-7989
16. G. K. Rao, A. Kumar, M. P. Singh, A. Kumar, A. M. Biradar, A. K. Singh, J. Organomet. Chem., 753 (2014) 42-47
17. S. A. Talouki, G. Grivani, P. Crochet, V. Cadierno, Inorg. Chim. Acta, 456 (2017) 142-148
18. W. A. Zoubi, Y. G. KO, J. Organomet. Chem., 822 (2016) 173-188

19. M. J. Reimann, D. R. Salmon, J. T. Horton, E. C. Gier, L. R. Jefferies, ACS Omega, 4 (2019) 2874-2882
20. N. Miyaura, A. Suzuki, Chem. Rev., 95 (1995) 2457-2483
21. K. Voronova, M. Purgel,́ A. Udvardy, A. C. Benyei,́ Á. Katho,́ F. Joo, Organometallics, 32 (2013) 4391-4401
22. L. Yu, X. Zhou, D. Wu, H. Xiang, J. Organomet. Chem., 705 (2012) 75-78
23. M. Allard, R. Ricoux, R. Guillot, J. P. Mahy, Inorg. Chim. Acta, 382 (2012) 59-64
24. X. Wang, G. Wu, F. Wang, K. Ding, F. Zhang, X. Liu, Y. Xue, Catal. Commun., 28 (2012) 73-76
25. P. Vanalabhpatana, D. J. Peters, Tetrahedron Lett., 44 (2003) 3245-3247
26. I. Correia, J. C. Pessoa, M. T. Duarte, M. F. M. Piedade, T. Jackush, T. Kiss, M. Margarida, C. A. Castro, C. F. G. C. Geraldes, F. Avecilla, Eur. J. Inorg. Chem., 4 (2005) 732-744
27. D. M. Boghaei, E. Askarizadeh, A. Bezaatpour, Spectrochim. Acta Part A, 69 (2008) 624-628
28. D. M. Boghaei, M. Gharagozlou, J. Coord. Chem., 60(3) (2007) 339-346
29. J. Zhou, X. Guo, C. Tu, X. Li, H. Sun, J. Organomet. Chem., 694 (2009) 697-702
30. C. Palopoli, N. Bruzzo, C. Hureau, S. Ladeira, D. Murgida, S. Signorella, Inorg. Chem., 50 (2011) 8973-8983
31. N. Shahnaz, A. Puzari, B. Paul, P. Das, Catal. Commun., 86 (2016) 55-58
32. J. Zhou, X. Li, H. Sun, J. Organomet. Chem., 695 (2010) 297-303
33. M. E. Hanhan, C. Cetinkayaa, M. P. Shaver, Appl. Organometal. Chem., 27 (2013) 570-577
34. V. A. Daier, C. M. Palopoli, C. Hureau, A. D. Candia, S. R. Signorella, Org. Chem. Argent., 7 (2011) 327-342.