

1.1. Introduction

The chiral molecules, which contain no internal mirror plane and S_n symmetry elements are unique in nature and some of them are most difficult to synthesize and purify. The two enantiomers may differ only in configuration of one atom, it may result in drastic impact in the way the molecule interacts with other chiral molecules such as protein in biological systems. It is known that one stereoisomer can be extremely effective against a disease where as the other can cause harmful effects. The production of enantiopure molecules is an important issue in the field of pharmaceuticals and agriculture, because of this, the food and drug administration recommends that in the case of chiral molecules the properties- particularly toxicity- of both enantiomers should be studied.^[1a] Hence, there is a continuous interest in synthesis of optically pure chiral compounds. Various strategies such as using chiral auxiliary, chiral pools and asymmetric catalysis have been employed. Of the all techniques used for enantioselective synthesis, asymmetric catalysis using transition metal complexes is found to be the most effective and widely used methods.

In the recent years there has been an immense interest in synthesis and characterization of metal complexes with chiral ligands.^[1b-d] This stems from the fact that such complexes can catalyze asymmetric synthesis which involves use of catalytic amount of metal complexes to give large quantities of optically pure organic compounds. In case of chiral metal complexes, the metal provides a center for catalytic activity, whereas the chiral ligand shoves an organic reaction to result in a strong bias to one enantiomer or the other. To accomplish highly enantioselective catalysis, the efficient ligand must be endowed with a suitable element of symmetry, substituents capable of differentiating the chiral molecule and capable of coordinating metal ion having catalytic activity for the desired reaction.

Hence for effective enantioselective catalysis by transition metal complexes, the consideration of basic principle of coordination chemistry is mandatory.

1.2. Coordination chemistry

The father of coordination chemistry, Alfred Werner defined basics of coordination chemistry, for which he was awarded the Nobel Prize in chemistry in 1913. The fundamental step was Werner's identification of two types of "valence". The 'first' he called a primary or ionizable valence (Hauptvalenz), presently known as oxidation state and the secondary or non-ionizable valence (Nebervalenz), now called coordination number. He postulated that every element tend to satisfy both, its Hauptvalenz and Nebervalenz. From this postulate, the concept of a fixed coordination number for a particular element in a particular oxidation state is arrived. Systematic investigations in the latter part of the 19th century provided a robust experimental basis for the study of coordination chemistry.

Werner published a very important observation that, as a consequence of an octahedral coordination geometry, tris(chelate) complexes must result in a chirality at the metal center. He denoted the enantiomers of complex cations as Δ and Λ referring to right and left handed enantiomers.

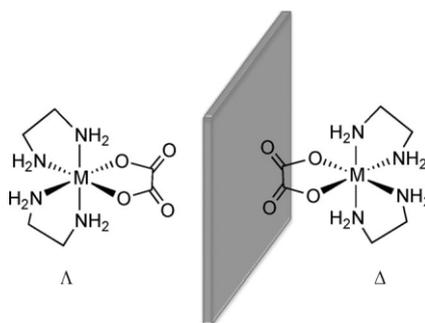


Figure 1.1 Tris chelate complexes are chiral and exist as two enantiomers which Werner managed to separate as diastereoisomeric salts with chiral anions.

As rightly reported by Constable and Housecroft it is the all-embracing structural theory of coordination chemistry, that is the real, and lasting legacy of Alfred Werner.^[2]

1.3. Ambiguity in assigning metal oxidation state

The oxidation state of transition metal in a transition metal complex is a central and often defining theme in coordination chemistry. In classical Werner type ligands the oxidation state of the metal complex is directly derived from the convenient basic rules for calculation of oxidation states. However this approach is not useful for the cases where the ligand is with molecular orbitals that are able to delocalize their electronic density to the metal center, a place where redox process can take place. Such ligands are with higher energy HOMO and lower lying LUMO compared to those of normal ligands. These ligands will therefore participate in electronic transfer, for such ligands Christian Jørgensen had coined the term “Noninnocent”.^[3]

The term “Noninnocent” has now, become synonymous with situations where the formal oxidation state, the one determined by a prescribed set of rules, diverse from an oxidation state that is determined by experiment.^[4]

It is reported by Richard Holm and Frank Neese that noninnocence is a state of ligand which under a particular situation behaves noninnocently.^[5]

Over the last five decades the field of Noninnocent redox active ligands has surged from a mere electronic structure curiosity to a diverse field of inorganic chemistry.^[6-10]

The importance of the field, noninnocent ligand is reflected in the survey of literature, as special issues related to the subject, have been published recently.^[11-13]

1.4. Some classical examples of Non-Innocent ligands

- Nitric oxide (NO) as non-innocent ligand.

The “brown ring” ion $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ formed in the analytical detection of nitrite or nitrate, on the basis of EPR and Mossbauer spectroscopy, is best described as $\text{Fe}^{\text{III}}/\text{NO}^-$ ^[13a]

In this case displacement of coordinated water followed by intramolecular charge – redistribution process on $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ by NO results in the formal oxidation of Fe^{II} to Fe^{III} and the reduction of NO to NO^- to form the final product $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_5(\text{NO}^-)]^{2+}$.

- **$\text{O}_2/\text{O}_2^{\cdot-}/\text{O}_2^{2-}$ as non-innocent ligand.**

Dioxygen, superoxide (hyperoxide radical anion) and peroxide have long been recognized as non-innocent ligands. The dioxygen non-innocent ligand system is distinguished by its capability to function beyond the $(\text{O}_2)^n$ states ($n = 0, 1-, 2-$) in a biochemical context. Three and four electron reduction of O_2 via O_2^{2-} by an oxidizable metal results in O–O bond cleavage to produce oxyl/hydroxyl ($\text{O}^{\cdot-}/\cdot\text{OH}$) radicals or oxide ions. The former is known as Fenton chemistry ^[14], mostly formulated as



- In addition to classical ligands NO and O_2 several other ligands have been recognized as redox-ambivalent as shown in the Figure 1.2 ^[13a,15,16]

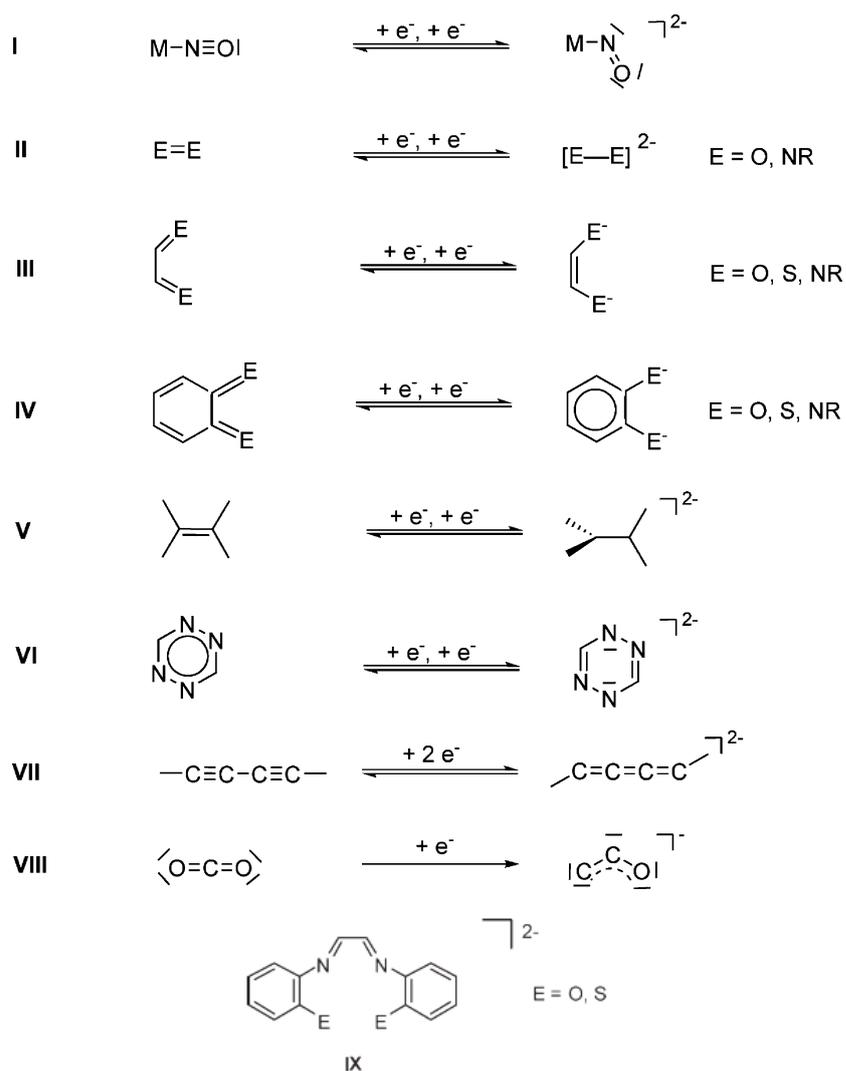


Figure 1.2 Examples of NILs

1.5. Classifications of NILs

The non-innocent ligands can be classified into different types, according to their behavior towards catalysis as shown in the flow chart. (Fig. 1.3)

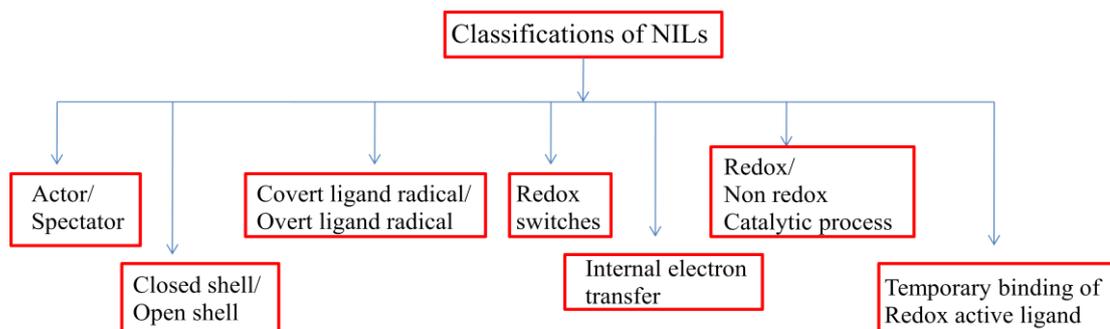
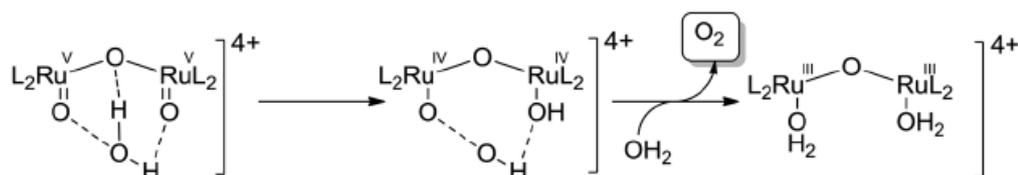


Figure 1.3 Classification of NILs

1.5.1. Actor ligand

Actor ligands are involved directly with the substrate during the catalytic reaction. Hurst et al. [17] have used ruthenium bipyridine complexes for oxidation of water where in ligand directly bind with substrate i.e. water. The proposed mechanism for the reaction is shown in Scheme 1.1.

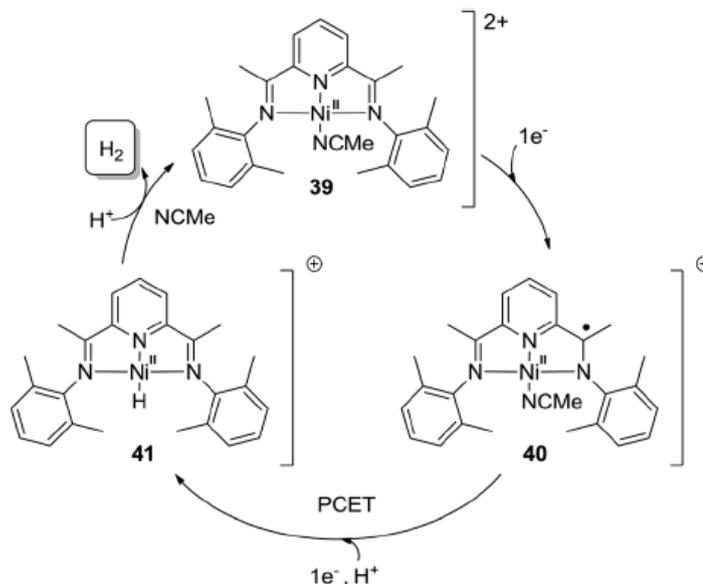


Scheme 1.1 water oxidation pathway with bimetallic ruthenium bipyridine complex

Spectator ligand

A spectator ligand exerts its effect on the metal that is the site of reactivity; such ligand may best be considered as a temporary location for storage of an electron or a hole. One of the example of this is Ni bis(iminopyridine) pincer complex.

Luca et al. ^[18] have used Ni bis(iminopyridine) complex for electrocatalytic hydrogen production. The proposed mechanism for this reaction is shown in Scheme 1.2.



Scheme 1.2 Proton reduction with a Ni bis(iminopyridine) complex

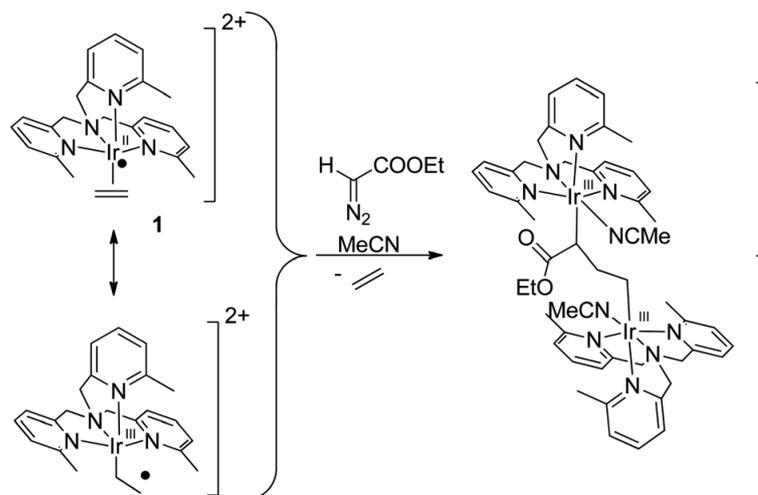
As can be seen from the Scheme 2, the ligand acts as an electron reservoir, stores the electron during catalytic process due to which no change in oxidation state of Nickel is observed throughout the reaction.

1.5.2. Closed shell redox activity

In closed shell redox activity, a ligand undergoes change in oxidation state by transfer of pairs of electrons in such a way that the system remains spin paired during the process. Wieghardt et al. ^[19] have synthesized Ni(II) complexes with *o*-catecholates, *o*-phenylenediamine, *o*-benzodithiolates, *o*-aminophenolates and *o*-aminothiophenolates and proved closed shell redox activity through DFT studies. A closed shell model, however assumes that a single HOMO is occupied by two electrons with antiparallel spin. In the **open shell case**, unpaired electron density is present at some stage.

1.5.3. Covert ligand radical

The term covert radical refers to the cases in which the ligand in the reactant complex is essentially spin paired but in the approach to the transition state for the reaction, the ligand acquires radical character so that it can give radical reactivity. (Scheme 1.3)



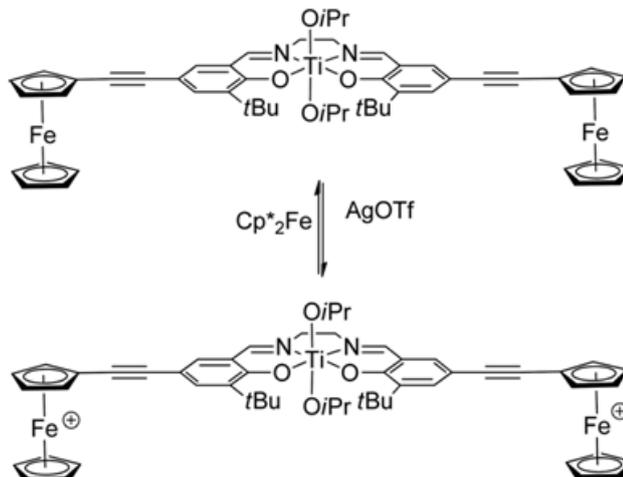
Scheme 1.3 Ir(III) carbenoid radical trapping

Here the reactant contains a metal centered radical but the chemistry implies the presence of ligand centered radical in the transition state. The term **overt ligand radical** simply refers to the more common case where significant unpaired spin density is present on the ligand.

1.5.4. Redox switches

Redox switches, involve a system with a ligand that adopt different oxidation states, one of which results in catalytic activity but the other gives a different catalytic activity or none at all. A possible application of this strategy would be the production of block copolymers, with the redox event switching the catalyst between two different modes of polymerization catalysis. Redox switching in single site lactide polymerization catalysts has been achieved by White and coworkers. (Scheme 1.4) ^[20]

They used Titanium salen complex whose oxidized species i.e. cationic counterpart inhibited the polymerization process while reduction reestablish the process.



Scheme 1.4 oxidation of titanium salen catalyst

1.5.5. Internal electron transfer

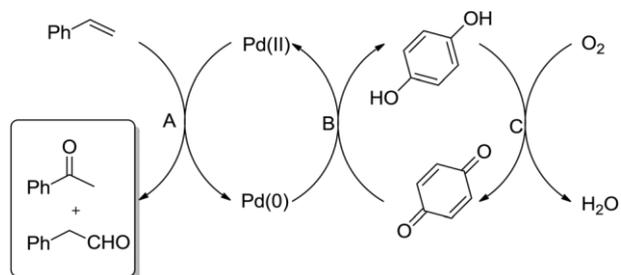
In internal electron transfer, the exchange of electron between metal and ligand takes place e.g. conversion of metal dihydrogen complex $M(H_2)$ to metal dihydride complex $M(H)_2$ or $Ir^V=O$ to $Ir^{IV}-O^\bullet$.

1.5.6. Redox active ligands engaged in a redox versus non redox catalytic process

In most of the cases redox active ligands are involved in redox catalysis, where the substrate is oxidized or reduced, but this is not always the case. On the other hand in the redox switched alkene polymerization, the catalytic reaction is itself redox-neutral, although initiated by redox change.

1.5.7. Temporary binding of a redox active ligand

The example of this type is modified Wacker reaction in which the redox active ligand 'quinone' binds only temporarily to Pd^0 to bring about the reoxidation of the metal that completes the catalytic cycle. (Scheme 1.5)



Scheme 1.5 Quinone mediated Pd catalysis in Wacker-type chemistry.

1.6. The present work

Nature has been the true pioneer of the noninnocent ligands. Metalloproteins contain metal ions such as iron and copper which preferentially react via one electron redox couples. However the important biological transformations like prostaglandin H synthase, Galactose oxidase and ribonucleotide reductase are multi electron processes which are carried out by noninnocent redox active ligands at the enzymatic active sites. [21,22]

Galactose oxidase (GAO) with phenolic oxygen system has been studied widely. [23-27] Many aminophenols have been proposed as models for GAO, wherein attempts have been made to prove the noninnocent nature of coordinated ligand.

Apart from acting as model for GAO, numerous chiral chelating amino phenols are reported as excellent ligands in metal ion catalyzed asymmetric reactions.

Among amino phenols **Betti base** (Fig. 1.4) and its derivatives have induced satisfactory reactivity and stereoselectivity in the auxiliary catalyzed asymmetric reactions.

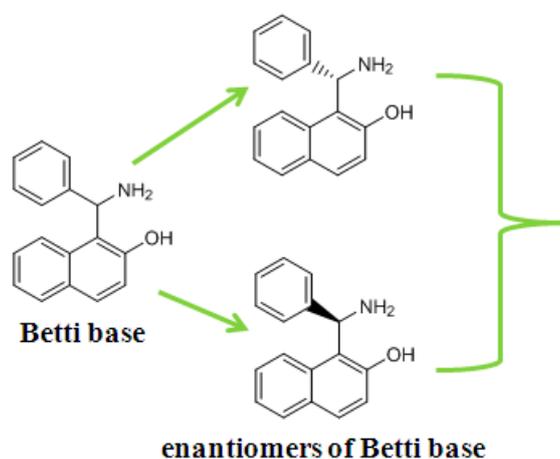


Figure 1.4 1-(α -amino benzyl)-2-naphthol (**Betti base**)

Betti base derivatives have provided convenient access to many useful synthetic building blocks via the amino and phenolic hydroxyl functional groups. [30-32] Optically active Betti bases complexed to dialkyl zinc have been used for enantioselective addition to aryl aldehydes. [32,33] Various applications [34] (Fig. 1.5) of

enantiopure amino naphthols as catalysts in stereoselective reactions have been reviewed by Fulop et al. [34] and Palmieri et al. [35]

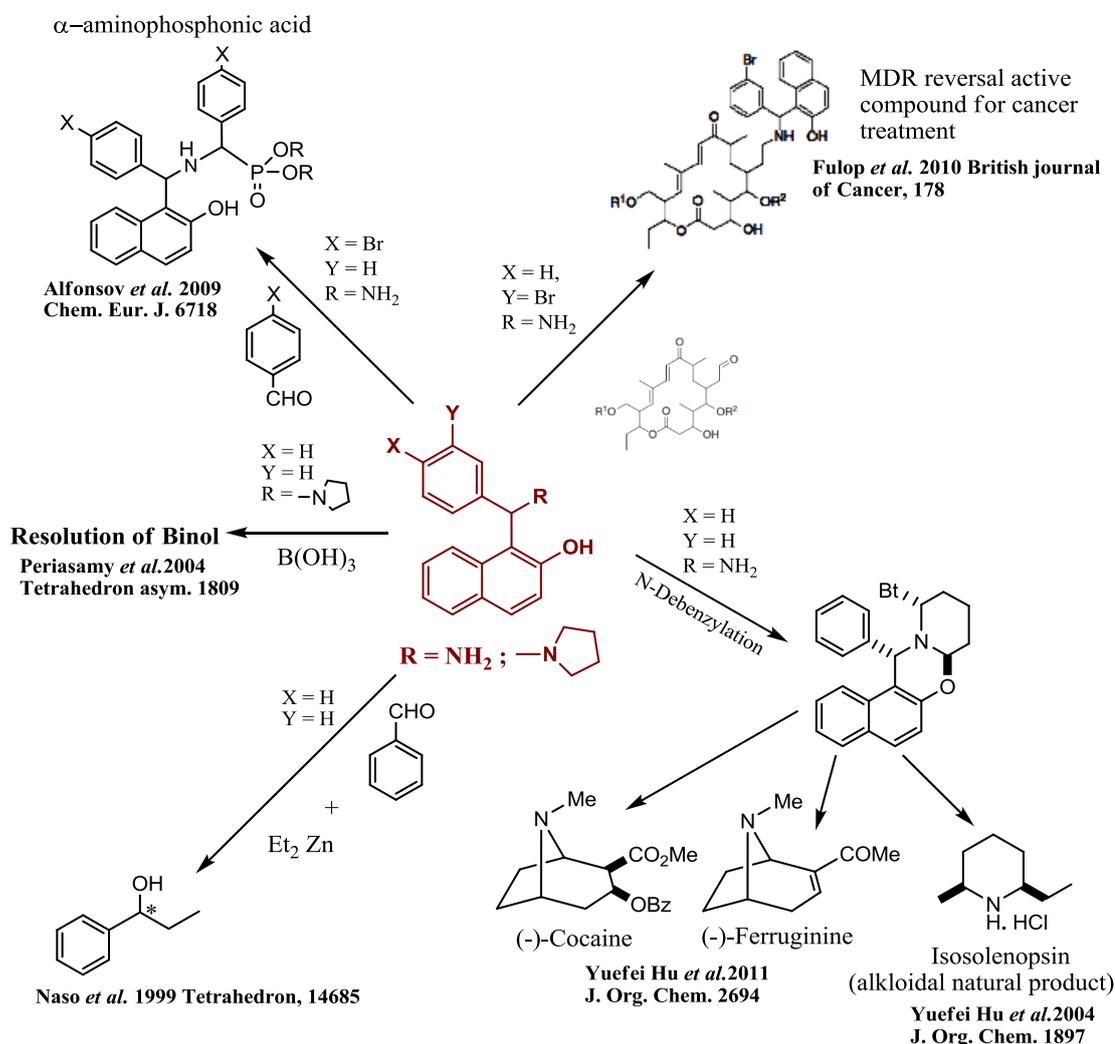


Figure 1.5 Applications of Betti base

Recently, a large library of aminonaphthylphenols obtained by the Betti reaction and their applications have been reviewed categorically by Naso and co-workers under the title of “The Betti base: the awakening of a sleeping beauty” [36]. In this review it is appropriately mentioned that, “in spite of the number of structures reported, that are important from the stereochemical point of view, and of the work performed so far, the synthetic potential of the Betti base family has been uncovered only to a small extent”. Betti base with sp³ hybridized carbon attached to phenyl ring, amine and naphthol, is expected to exhibit interesting redox properties. Also with

phenolic–OH and amino groups it is expected to act as an excellent ligand for coordination with transition metal ions.

1.7. The aim of the present work

To prove that

- **Betti base and its derivatives exhibit Noninnocent behavior when coordinated with metal ion and catalyze redox reaction involving two electron transfer.**
- **Cu(II) complexes with chiral Betti base should induce enantioselectivity to the catalytic product.**

1.8. Methodology

In order to achieve the above aim the research work was planned as follows

- Synthesis of optically active Betti base and its analogs by reported methods.
- Synthesis and characterization of transition metal complexes.
- Electrochemical study of the ligand and metal complex in order to prove Noninnocent behavior of the ligand.
- Application of resulting complexes as a catalyst for two electron transfer reaction, asymmetric epoxidation of styrene.
- Application of metal complexes for stereoselective cyclopropanation of styrene.

1.9. Presentation of the work

The work carried out is presented as follows

- 1) Synthesis, characterization and electrochemical properties of Betti base and its derivatives. **Chapter 2** deals with the details and conclusion of the work.
- 2) **Chapter 3** deals with the synthesis, characterization and electrochemical properties of Cu(II) complexes with Betti base and its derivatives.
- 3) In the **chapter 4**, the work related to cooperative catalysis with Cu(II) complexes with Betti bases is presented.
- 4) **Chapter 5** is related to the study of catalytic activity of Cu(II) complexes with Betti base for cyclopropanation of styrene.

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