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Pyridine and Related Ligands in Transition Metal Homogeneous Catalysis[1]

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Abstract—This review provides a broad overview of the literature related to the importance of pyridine and related ligands in homogeneous catalysis. In particular, it describes the various ways by which this ligand can stabilised the metal within a complex for homogeneous catalysis. We surveyed the important transition metal homogenous catalysts containing pyridine and related ligand acting as backbone for other ligands in homogeneous catalytic reactions explicitly from 2011 up to early 2014 and summarized their comparative catalytic activities.

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INTRODUCTION

Inorganic chemists face significant difficulties in the design and production of industrial catalysts with broad applicability. High-throughput experimentation and combinatorial chemistry have been set forward as promising avenues to expedite catalyst development processes [1–5]. The stability and the selectivity of a homogenous catalyst are strongly related to its molecular structure as well as size, bonding and secondary interaction of ligands with metal. The stability of molecular structures with pyridine as supporting ligand is very successful approach in homogenous catalysis. Other ligands with pendant pyridine arms are not only helpful in fulfilling the secondSary valency of metal but also helpin bringingother ligandsin close proximity of central metal that helps in rapid formation of metal complexes.

There are not many examples that used free pyridine as auxiliary ligand in metal complex homogeneous catalysis from 2011 to early 2014. In 2012, A. Carla and its co-workers synthesized molybdenum(II) tricarbonyl complex [$Mo(CO)_3I_2$(2,2-Bipy-4,4-di-*t*-Butyl-2,2-Bipy)] (**I**), where 2,2-Bipy is 2,2-bipyridine, *t*-Bu is *tert*-butyl. It was used as catalyst precursor to oxomolybdates(VI) catalyst for selective epoxidation of methyloleate (MO) to yeild methyl-9,10-epoxystereate (MES) in the presence of tertiary butylhydroperoxide (TBHP) (Scheme 1) as oxidant. The reaction was carried out at 75°C with Mo : MO : TBHP molar ratio of 1 : 100 : 152 gave MES in 70% yield. It was found out that the presence of tertiary-butyl substituent in the aromatic ring increases the reaction rate. The mechanism involve the oxidative decarbonylation and loss of the iodo ligands that result in one dimensional molybdenum oxide/bipyridine polymer [MoO_3(2,2-Bipy)], octanuclear [Mo_8O_{24}(4,4-di-*t*-Bu-2,2-Bipy)$_4$] and pyridinium-β-octamolybdates (H-pyridine)$_4$[Mo_8O_{26}]. By using catalyst precursors containing Mo(II) the epoxidation selectivity was reduced but as the recovered catalyst containing Mo(VI), in second run, the epoxide selectivity was found to be greater, i.e. 99% [6].

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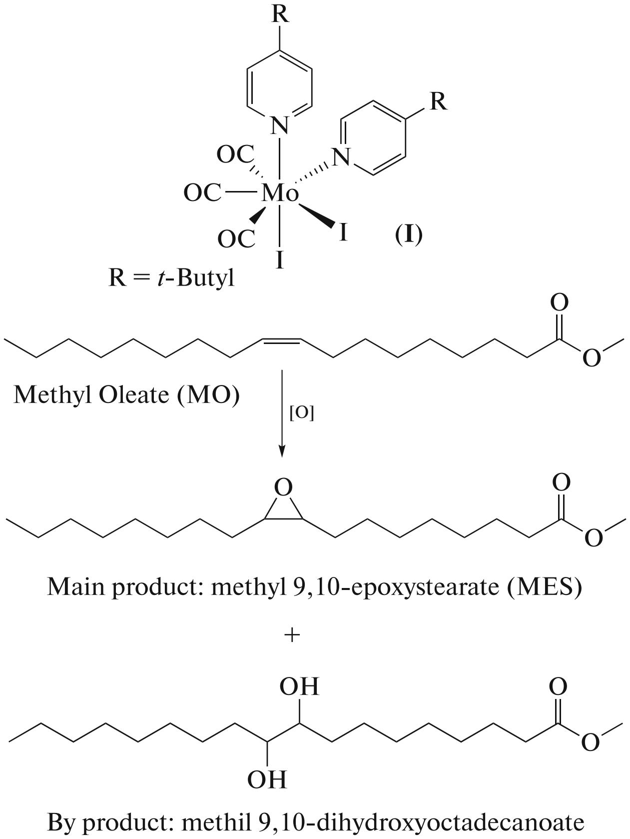
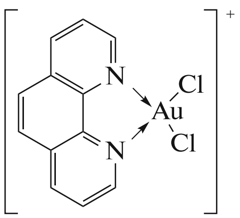


(Reaction of MO with TBHP at 75°C using catalyst precursors)

Scheme 1.

EXTENDED AROMATIC PYRIDINE RINGS

The use of extended bidentate aromatic pyridine rings in which either pyridine rings connect with each other directly or via another non-pyridyl aromatic ring is regular in homogeneous catalysis. For example, phenanthrolinebidenatate aromatic ligand was used by Jinjin Li and its co-workers in 2011 to synthesize a catalyst **II**. Organic carbonates were produced most favorably by carbonylation of alkyl nitriles. The catalyst used in this reaction is $[AuCl_2(Phen)]Cl$ (Phen = 1,10-phenanthroline) and KI was used as promoter. The catalyst was prepared by adding a 10 mL ethanolic solution of 1 g $HAuCl_4$ into 10 mL ethanolic solution of 1 g of ligand with stirring and heating continuously for several hours as to get a yellow to orange precipitates which were cooled to room temperature and washed with ethanol and then dried. When KI was added in the solution, Cl of catalyst was replaced by I, this was done because iodide is a good promoter in most of the carbonylation reactions as compared to Cl. The experiment done for converting alkyl nitrile to alkyl carbonate in the presence of this catalyst is performed in a stainless steel autoclave equippment of 100 mL with a mechanical stirrer [7]. Similarly in 2012, Goldsmith synthesized phenanthroline based dichloro-bis[(1,10-phenanthroline)]gallium(III) complex (**III**). This complex catalyzed the alkene epoxidation by using peracetic acid. Catalytic reaction proceeded at a very low temperature and more quickly due to the existence of neutral and electron deficient phenanthroline ligands that bounded to the gallium during the homogeneous catalytic process. Alkenes bearing more electron deficient terminals reacted less efficiently which was proved by lesser yield of epoxides. The more electron poor ligands promoted considerable epoxidation of alkenes, such as in case of $[Ga(Phen)_2Cl_2]Cl$ complex [8].



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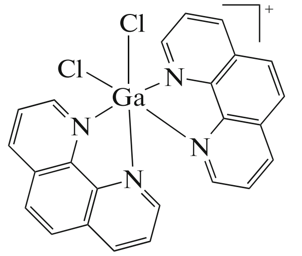
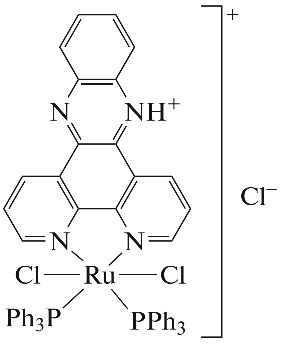


(III)

In 2012, Moya and Aguirre synthesized ruthenium complex Ru(Dppz-Cl)(Pph$_3$)$_2$Cl$_2$ containing polypyridine ligand acted as an active catalyst for the transfer hydrogenation reaction of N-benzylideneaniline **(IV)**. Polypyridine ligand stabilized the metal in the catalytic reaction because the triphenylphosphine increased the electronic density on the metal. The metal hydrogen intermediate was formed due to the presence of donor ligands. This catalyst containing Dppz-Cl ligand reacted more rapidly with the acidic metal hence yield of the product enhanced. In short reaction time high selectivity was observed. The yield was reported as 75, 83, 85, 88% in 30, 60, 90 and 20 min, respectively [9]. Mckenzie synthesized in situ the palladium complex **V** which is suitable for catalysis of allylic substitution reactions [10].



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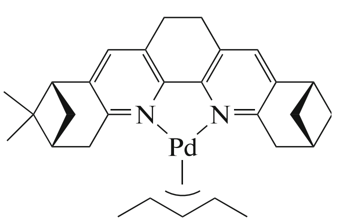
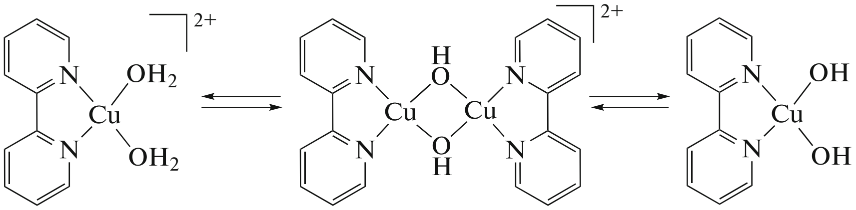


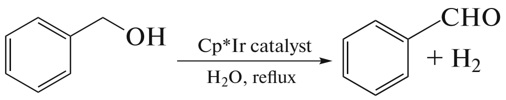
(V)

In 2012, M.B. Shoshanna and R. Kawahara independently reported the bipyridyl based complexes in homogenous catalysis. M.B. Shoshanna published first homogeneous copper electro-catalyst for water oxidation to molecular oxygen (Scheme 2). This catalyst is really attractive target for water oxidation because of its biomimetic chemistry with oxygen as in nature nitrogen ligated copper(I) reacted readily with oxygen molecule to give monomeric and peroxo complexes. This complex is cheap and self assemble from simple commercial material in aqueous solution at high basic pH ranging 11.8–13.3. It has turnover frequency of the 100/s and catalysis occur at about 750 mV over-potential. Salts of diametric bis-μ-hydroxide cation $[(\mathrm{Bipy})\mathrm{Cu}(\mu\text{-OH})]_2^{2+}$ were isolated readily from the alkaline solutions of 1 : 1 Cu^{2+} and Bipy. Cyclic voltamograms (CV) was obtained under working electrode of ITO and GC. After scanning at 100 mV a large irreversible wave was observed at –0.3 V due to O_2/O_2^- production by the oxidative catalysis. Production of dioxygen at +1.35 V on ITO was measured during controlled potential electrolysis then in 30 min the dissolved oxygen concentration rose from 10 to 330 μmole as compared to 110 μmole in the absence of copper, after 30 turnovers only 35% decomposition of catalyst held. Cu specie was found to be fast, soluble water oxidative catalyst. At higher pH more catalytic current was produced but at lower pH non catalytic copper equilibrium exist [11]. The electro-catalysis reaction based on 4-electron process is shown in Scheme 3. In 2012 R. Kawahara synthesized catalyst Cp*Ir bearing bipyridine functional group **(VI)**. This catalyst was highly soluble in water and was stable in air for months. It was used in dehydrogenative oxidation of benzyl alcohol to form benzaldehyde (Scheme 4) with no oxidant used. This catalyst showed excellent results with yield 92% having complete selectivity but this process required catalyst in high amount (1.5 mole % Ir). It was also found that this reaction works equally well under air and under argon atmosphere and gave similar products which showed advantage of this catalyst. The reaction of benzylic alcohol having electron donating, electron withdrawing group, sterically hindered and unhindered substrate gave high yield. Similarly oxidation of secondary alcohol to acetophenone was also obtained in high amount. The highest turnover number 2550 was obtained under reflux for 100 hours with very small catalyst amount (0.02 mol %) in aqueous media. This catalyst was recycled by using hexane so it could be used for further reactions. From the point of green chemistry, it was advantageous to use this catalyst as this catalyst gave its catalytic activity in the presence of green solvent like water which is harmless solvent and reaction proceeded without formation of any harmful byproducts 12].



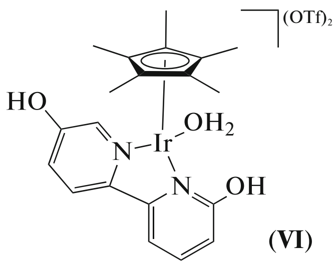
(The aqueous speciation of 1 : 1 copper(II) : Bipy solution, by EPR)

Scheme 2.



(Dehydrogenative oxidation of benzyl alcohol using Cp*Ir catalyst)

Scheme 3.



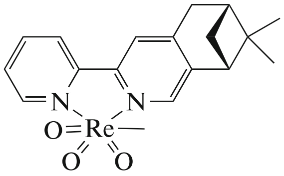
(VI)

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

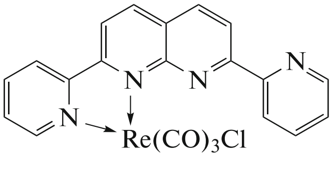
(Electro-catalysis reaction)

Scheme 4.

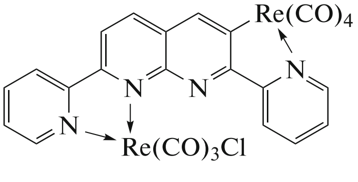
Rudler studied the epoxidation of olefins and found that methoxytrioxorhenium (**VII**) catalyses the selective epoxidation of alkenes [13]. In 2013, Liu synthesized two complexes **VIII** and **IX** from pyridinyl-naphthyridine ligand with rhenium metal. Catalytic activity of these complexes in insertion of alkynes into β-keto esters (which afterwards converted to 2-pyranones by cyclization process) was observed. Complexes **VIII** and **IX** gave 53 and 84% yield, respectively. Cyclization process was promoted by tetrabutylammonium fluoride (TBAF) [14].



(VII)

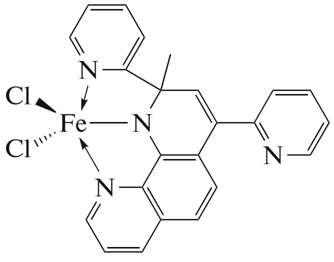


(VIII)

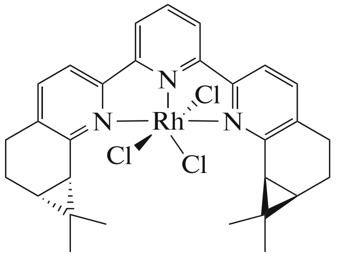


(IX)

Tridentate ligands with all three rigid aromatic arms of either pyridine or pyridine type ligands were greatly explored in homogenous catalysis in last four years. A. Boudier with co-workers in 2011 prepared Fe(III)-based complex with 2-methyl-2,4-bis(pyridin-2-yl)-1,2-dihydro-1,10-phenanthroline. The ligand was prepared by condensation of 8-aminoquinoline with 2-acetylpyridine. The catalyst **X** was obtained by deprotonation of ligand with *n*-BuLi followed by addition of $FeCl_3$ in THF solvent. This catalyst was used for the oligomerization of ethylene to obtain linear α-olefins (LAOs) having smaller chain length (C_4–C_{10}) [15]. Chelucci synthesized the rhodium terpyridine complex **XI** and used it in the catalytic cyclopropanation of styrene [16].

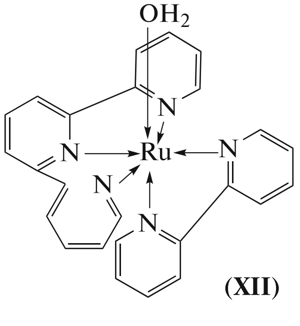


(X)



(XI)

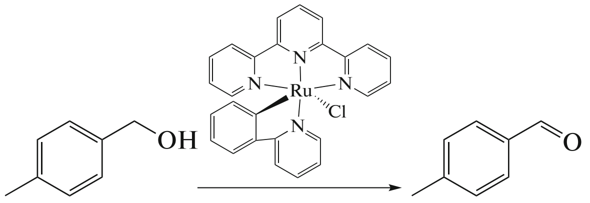
In 2012, T. Kanbara with co-workers studied aerobic oxidative dehydrogenation of benzyl alcohols to benzaldehydes by using a cyclometalated ruthenium catalyst (Scheme 5). These ruthenium(III) phenylpyridine complexes are also effective catalyst for aerobic hydrogenation of benzylamine and alcohol. The most important feature of this catalyst is σ-donor ability of N-donor ligand that enhances aerobic oxidation. One of the necessary condition for this reaction is that catalyst should have low oxidation potential and this ruthenium(III) specie has this ability. This complex can also undergo oxidation of benzyl alcohol into benzeldehyde without over-oxidation. Catalytic activity can be increased if reaction is carried out in presence of oxygen and yield is increased from 5 to 80% [17]. Yagi with co-workers (2011) reported their work in artificial photosynthesis for evolution of O_2 from water by using mononuclear ruthenium(II) monoaquo complexes **(XII)**



(XII)

(Re = H, EtO, MeO, Me)

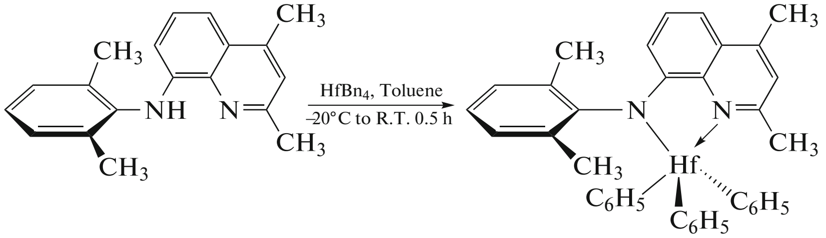
They attempted to develop an efficient catalyst by chemical modification of $[Ru(Tpy)(Bipy)OH_2]^{2+}$ (Tpy = 2,2':6',2''-terpyridine) which was well-established to be oxidized to $[Ru(Tpy)(Bipy)(O)]^{2+}$ by proton-coupled electron transfer in which nitrogen was acting as electron donor. They synthesized a series of these complexes and demonstrated that their catalytic activities can be tuned by chemical modification of Tpy ligands. They also reported $[Ru(EtOTpy)(Bipy)OH_2]^{2+}$ as a new catalyst for water oxidation with the significantly high O_2 yeild (K_{O_2} = 1.1×10^{-1} s^{-1}). The introduction of an EtO group to the 4-position on Tpy for $[Ru(RTpy)(Bipy)OH_2]^{2+}$ complexes made the Ru–N and Ru–O bonds significantly longer. In order to show the catalytic activity of a series of $[Ru(RTpy)(Bipy)OH_2]^{2+}$ complexes, homogenous catalysis experiments were performed by using Ce(IV) as oxidant (Scheme 6). The amount (nO_2/mol) of O_2 evolved increased linearly with time until 100 min and then saturated to 35 mmol at 4 h. In that case, the turnover number (TON) was 350. It was likely that an O–O bond was formed by coupling of Ru(V)=O with outer-sphere water for O_2 evolution. The pK_a values revealed that high basicity of an aquooxo might be important for the high catalytic activity [18].



Yield 92%

(Aerobic oxidative dehydrogenation of benzyl alcohols to benzaldehydes using ruthenium catalyst)

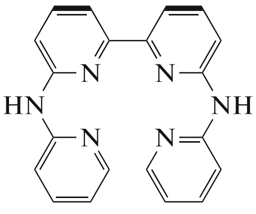
Scheme 5.



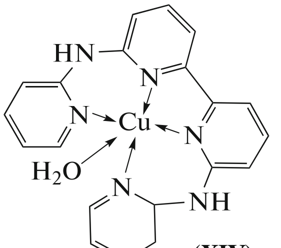
(Metallation of aminoquinoline ligand)

Scheme 6.

In 2013, tetra- and pentadentate pyridine ligands **XIII** were explored. Bonnet and its co-workers synthesized copper complex $[Cu(BapBipy)(H_2O)]Cl_2 \cdot H_2O$ **(XIV)** with neutral N-donor ligand having distorted square pyramidal geometry with N atoms at equatorial positions and water molecules at apical position.

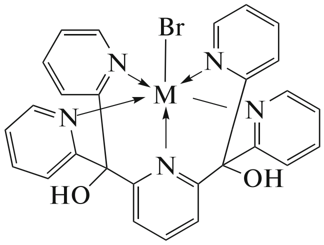


BarBipy **(XIII)**



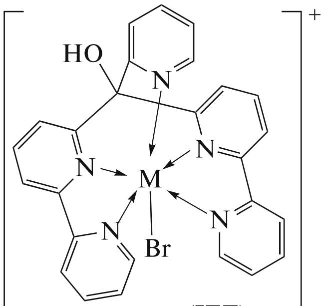
(XIV)

This copper complex was used as catalyst in aerobic oxidation of benzyl alcohol to benzaldehyde in 44% yield (not converted to benzoic acid) using (2,2',6,6'-tetramethylpiperidin-1-yl)oxidanyl. Catalytic activity of the ionic species was shown in methanol–acetonitrile [19]. Roger Alberto with co-workers in the same year reported water reduction Mn(II), Fe(II), Co(II), Ni(II) catalysts as $[MBr(1)]^+$ & $[MBr(2)]^+$. Cobalt and nickel complexes gave better results for photocatalytic water reduction. High electro and photocatalytic reactivity was shown by cobalt complexes with polypyridyl ligands. Penta-pyridyl ligand having five pyridine units and two hydroxyl functions **(XV)** and another ligand having two 2,2'-Bipy and single pyridyl donor **(XVI)**.



(XV)

M = Mn, Fe, Co, Ni, Cu, Zn



(XVI)

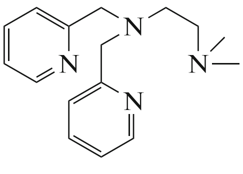
M = Mn, Fe, Co, Ni, Cu, Zn

Complex **XVI** was not ideal for pentadentate coordination ligand and had one pyridine and two bipyridine subunits oriented in tetrahedral manner to lower the steric interactions so complex structure was distorted from octahedral geometry as a result the complex was less stable and showed high reactivity. These complexes showed catalytic activity in water only when ascorbic acid was present. The photocatalytic water reduction activity of **XVI** was greater than **XV** [20].

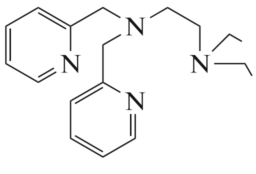
USE OF RIGID PYRIDINE AS BACKBONE FOR OTHER LIGANDS IN HOMOGENOUS CATALYSIS

Pyridine Arm Supporting a Ligand Functionality

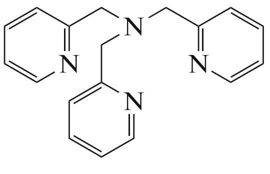
Pyridine support amine. In 2011, Balamurugan with co-workers synthesized many complexes of type $[Ni(L)(CH_3CN)_2](BPh_4)_2$ having distorted octahedral coordination geometry with various tetradentate tripodal 4N-ligands (L = **XVII–XXI**). All these catalysts were used in the oxidation of alkanes, such as cyclohexane, cumene, adamantane, ethylbenzene in the presence of *m*-chlorobenzoic acid (*m*-CPBA) used as oxidant. The catalyst with ligand **XVII** gave maximum yield of 62.2, 44.3, and 43.8% with TON 622, 443, and 438 towards the oxidation of cyclohexane, ethylbenzene and cumene, respectively. In case of oxidation of adamantane, catalyst with ligand **XVIII** gave maximum yield of 65.6% with TON 656 [21].



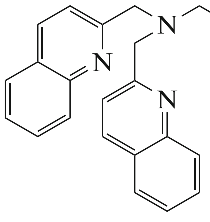
(XVII)



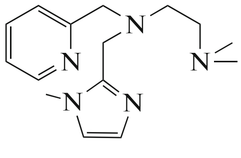
(XVIII)



(XIX)

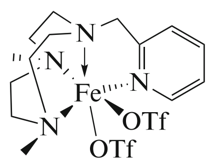


(XX)



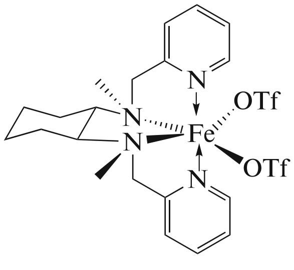
(XXI)

In the same year, Costas with co-workers synthesized a number of iron complexes containing tetradentate nitrogen based ligands (**XXII–XXVI**).



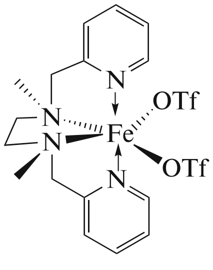
[Fe(OTf)$_2$(Pytacn)]

(XXII)



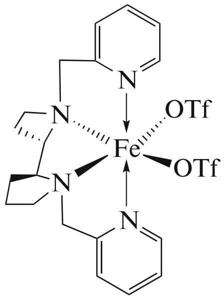
[Fe(OFt)$_2$(Mcp)]

(XXIII)



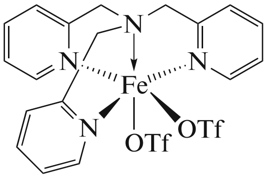
[Fe(OTf)$_2$(Bpbp)]

(XXIV)



[Fe(OTf)$_2$(Mep)]

(XXV)



[Fe(OTf)$_2$(Tpa)]

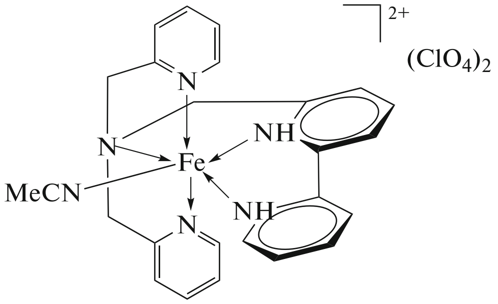
(XXVI)

Pytacn = 1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane,
Mcp = *N*,*N*-dimethyl-*N*,*N*-bis(2-pyridylmetyl)-cyclohexane-1,2-diamine,
Bpbp = *N*,*N*-bis(2-pyridylmethyl)-2,2/-bipyrrolidine, Mep = *N*,*N*-dimethyl -
N,*N*-bis-(2-pyridylmethyl)-ethane-1,2-diamine, Tpa = tris-(2-pyridylmethyl)amine

These amine-pyridyl based ligands stabilized metal centres in high oxidation states and shared a common tetradentate coordination arrangement to the metal centre i.e. they gave two relative *cis* labile sites, an important structural feature of a catalyst for eliciting water oxidation. These iron complexes catalyzed homogeneous water oxidation most efficiently with TON > 350 using cerium ammonium nitrate and

>1000 for sodium periodate as oxidant at pH 1 and 2, respectively. These activities of iron based catalysts were the highest for homogeneous catalytic system than for any other first row transition metal uptill 2011. The activities of Fe complexes were very close to that of highly active ruthenium and iridium based catalytic system but the high toxicity and price of Ru and Ir limit their extensive use as compared to iron which is non-toxic and abundant [22].

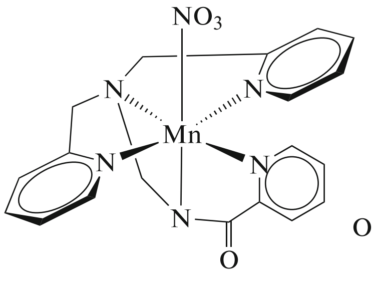
In 2013, E. Wong with co-workers, isolated and characterized iron(IV)-oxo complexes bearing tetradentate and pentadentate ligands. The tripodalpentadentate ligand synthesized by the reductive amination of 2,2'-bipyridine-6-carboxaldehyde with bis(pyridylmethyl)amine in which the catalytic amount of thionyl chloride was added. The quantitative yield of iron complex **(XXVII)** was obtained by the reaction of ligand in acetonitrile with one equivalent of iron(II) perchlorate.



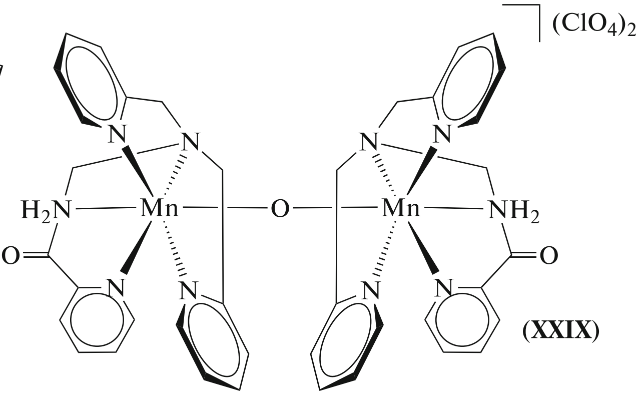
(XXVII)

The resulting red complex had low spin due to intensive red color of complex which was expected from strong ligand field generated by four pyridine donors, one amine and one acetonitrile ligand. The six *d*-electrons were paired in iron(II) complex, provided by highly conjugated nitrogen donor ligands. A strong ligand field contributed in the stabilization of Fe(II) oxidation state. The iron(IV) oxo species were short lived formed by the the reaction of $[Fe(L)(CH_3CN)](ClO_4)_2$ with PhIO to form stable oxo-bridged iron(III) complex. The catalytic properties of complex $[Fe(L)(CH_3CN)](ClO_4)_2$ had been evaluated for the oxidation of cyclohexane with H_2O_2 but it showed moderate catalytic activities [23].

Pyridine support amine and amidate. Complexes containing pyridine amidate ligands have been much less studied than those containing amido or amine ligands. In 2013, Brudvig studied four different manganese complexes of pentadentate ligands. Two of them, $[Mn(PaPy_3)(NO_3)](ClO_4)$ **(XXVIII)** and $[Mn(PaPy_3)(\mu\text{-}O)(PaPy_3)Mn](ClO_4)$ **(XXIX)**, were anionic.



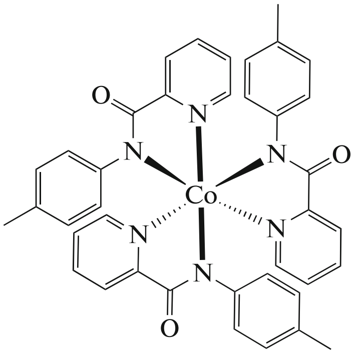
(XXVIII)



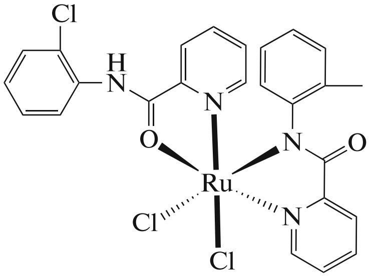
(XXIX)

These two anionic carboxamido ligands when attached *trans* to labile sixth coordinate position act as catalyst and released oxygen having oxone or hydrogen peroxide in the reaction and high valent metal structures formed. The catalytic structure was not lost when it was used instead of μ-oxo ligands [24].

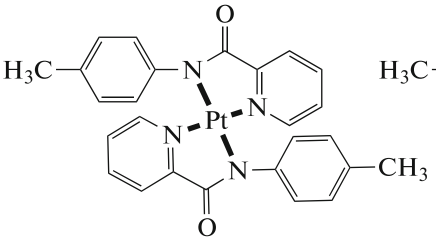
Pyridine support amidate. Chan have reported the synthesis and characterization of a trivalent cobalt complex (**XXX**) containing a pyridine carboxamide ligand [25]. The complex was found to be highly active and remarkably selective in the oxidation of ethylbenzene to acetophenone using dioxygen as the oxidant and demonstrated the usefulness of pyridine carboxamide metal complexes in oxidation catalysis. Chan have also reported chemistry of ruthenium complexes (**XXXI**) with pyridine carboxamide ligands and found them as highly efficient catalyst in epoxidation of cyclic alkenes [26]. Guohave synthesized three novel platinum(II) complexes (**XXXII–XXXIV**) using pyridine carboxamide ligands, which were found to have antitumour properties [27]. Another application in biological systems can be found in a report by Olmstead who investigated the behaviour of pyridine carboxamide ligands towards the biologically relevant d-block metal copper as model compound (**XXXV**) in biological systems [28].



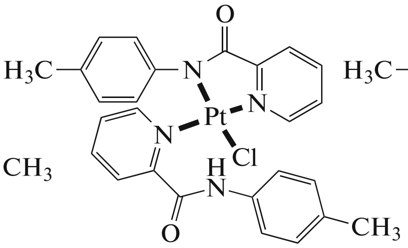
(XXX)



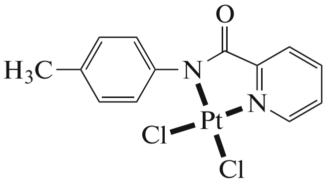
(XXXI)



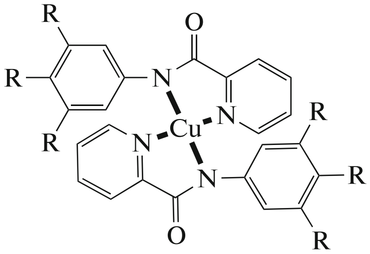
(XXXII)



(XXXIII)

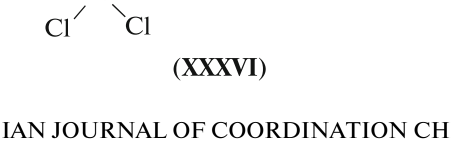


(XXXIV)



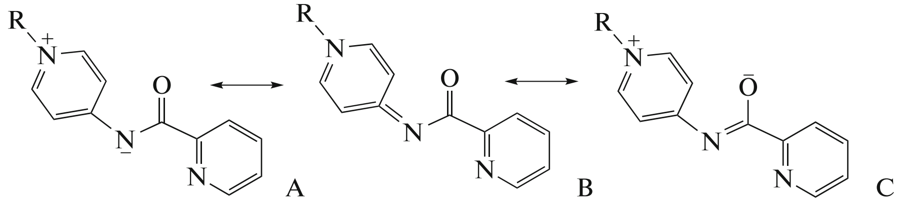
(XXXV)

Pyridine support pyridinium amidate (PYAs). In 2011, we have successfully used pyridinium amidate based ligand to form complex **XXXVI** in C–C Suzuki and Heck coupling reactions [29].



(XXXVI)

Pyridinium amidate is a set of ligands that share the common features of neutral overall charge and one valence bond representation in which the donor atom is negatively charged but is in π conjugation with a positively charged "iminium-like" group. Examples of classes of ligands with these features are NHCs, "remote" NHCs, and the recently reported *N*-[1-alkylpyridin-4(1*H*)-ylidene]amines (PYEs). The electron donor property and *trans* influence of these type of ligands is similar to NHCs and PYEs. The structures A, B and C in Scheme 7 show the resonance forms of PYA. In view of the strong σ-donor characteristics, ease of synthesis, and relative stability of these ligands, it can be anticipated that future applications might be found in numerous other catalytic systems.

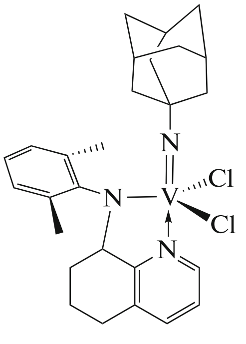


Pyridinium amidate *N*-(1-benzylpyridin-4(1*H*)-ylidene)picolinamide O-Pyridinium amidate

(Resonance structures of PYA (R = CH_3, Bu))

Scheme 7.

Quinoline support amido. Tang (2014) studied a catalyst (imido)vanadium(V)dichloride complex containing 8-(2,6-dimethyl(anilide)5,6,7-trihydroquinoline ligand **(XXXVII)**.



(XXXVII)

The geometry of complex was trigonal bipyramidal. The complex was used for ethylene dimerization. The catalyst showed catalytic activity in dimerization of ethylene in the presence of MAO (methyl aluminium oxide co-catalyst) used in excess. Three complexes with different R group were obtained which possesed different selectivity for ethylene dimerization. The higher selectivity was shown by complex containing R (admentyl group) with up to >90% ethylene dimerization. The $V(NAd)Cl_2[8\text{-}2,6\text{-}Me_2C_6H_3)N(C_7H_{10}N]$ complex showed remarkable catalytic activity resulting in 1-butene 9600000 h^{-1}. The imido ligand and chelate donor ligand in this complex showed high reactivity with high selectivity for the dimerization process [30].

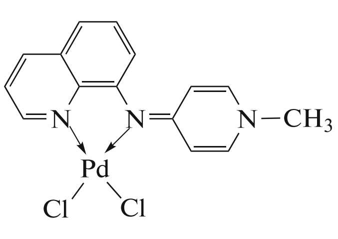
Quinoline supported amidohafnium complex was synthesized by Fontaine and its co-workers in 2012 by stirring the aminoquinoline with tetrabenzylhafnium in the solution of toluene. X-ray crystallography showed that all the hafnium complexes show trigonal bipyramidal geometry. Coordination of two nitrogen donor ligands to hafnium results in the formation of the complex ((2,6-dimethylphenyl)(2,4-dimethylquinolin-8-yl)amino)-tribenzylhafnium, 5-membered metallacycle (Scheme 8) due to this reason, these complexes provide rigid structure and hence rearrangement does not occur in these complexes at elevated temperature. This complex was highly active for ethylene–1-octene copolymerization at 120°C [31].

$$4H_2O + Ce^{IV} \xrightarrow{[Ru(Tpy)(Bipy)OH_2]^{2+}} O_2 + 4Ce^{III} + 4H^+$$

(Water oxidation catalysis using ruthenium catalyst and Ce(IV) oxidant)

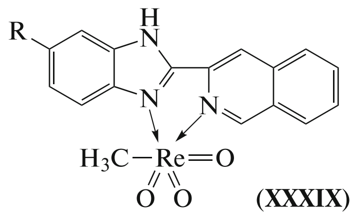
Scheme 8.

Quinoline support pyridinium amide. In 2011, we synthesized pyridinium amide based palladium complex $[Pd(PYE)Cl_2]$ **(XXXVIII)** with protonated pyridinium amide ligand (H-PYE). H-PYE was treated with $[Pd(COD)_2Cl_2]$ precursor in the presence of DBU to in situ generate PYE ligand in refluxing dichloromethane for 2 h. The complex generated was used for Heck and Suzuki coupling reactions and was compared with analogues palladium pyridiniumamidate complex $[Pd(PYA)Cl_2]$. It showed that $[Pd(PYA)Cl_2]$ is better ligand than $[Pd(PYE)Cl_2]$ for these type of coupling reactions [29].



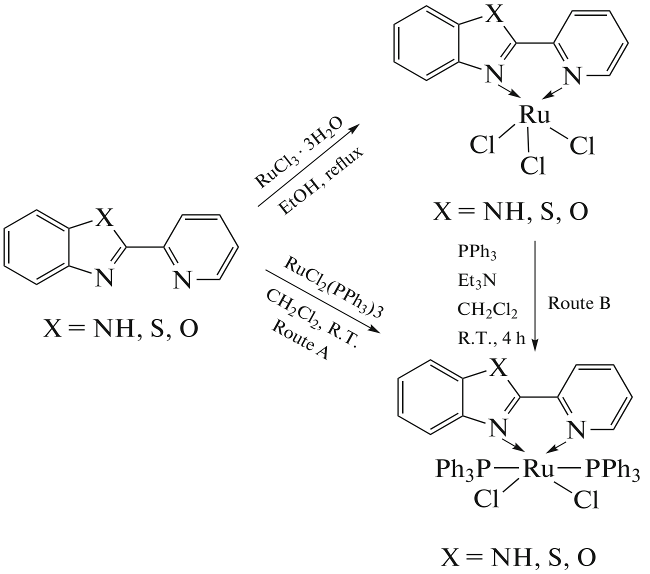
(XXXVIII)

Pyridine support azoles. Ojwach (2014) reported (pyridyl)benzoazole Ru(II) and Ru(III) complexes for transfer hydrogenation of ketones in catalytic cycle. The complexes with X = N–H (Scheme 9) had greater catalytic activity than O and S ligands [32]. In 2013, E. Kuhn and his co-workers synthesized benzimidazolic complexes of methyltrioxorhenium(VII), for example, complex **XXXIX**:



(**XXXIX**)

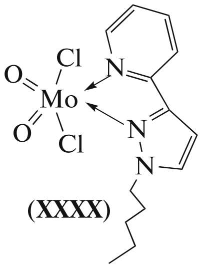
R = H, Me, Cl



(Synthesis of Ru(II) and Ru(III) catalyst)

Scheme 9.

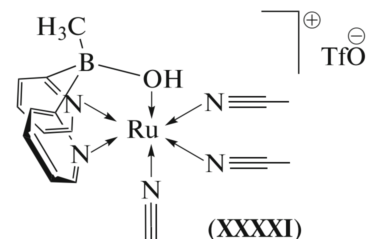
These complexes were able to live for several days in air. They act as a god catalyst for olefin epoxidation in the presence of hydrogen peroxide as oxidant [33]. S. Goncalves (2014) reported the preparation of a catalyst dioxomolybdenum(VI) [MoO_2Cl_2(Pent-pp)] complex (**XXXX**) by the reaction of solvent adduct [$MoO_2Cl_2(THF)_2$] with 2-(1-pentyl-3-pyrazolyl)pyridine.



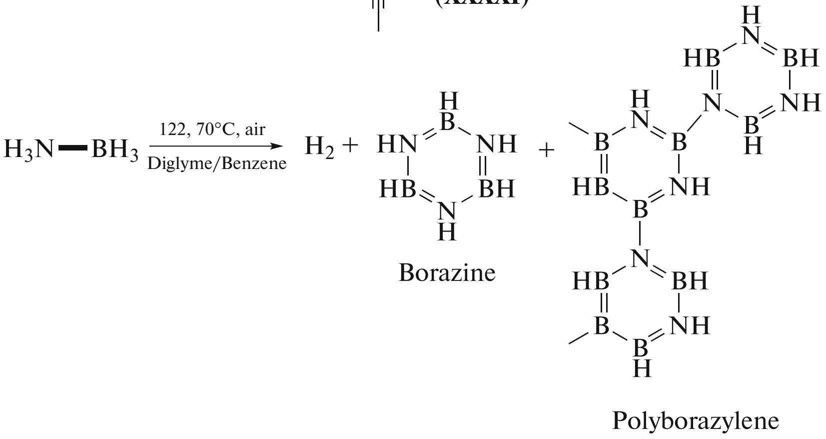
(**XXXX**)

In this complex, molybdenum was coordinated with nitrogen and geometry of complex was octahedral. These complexes were used as catalysts for epoxidation of *cis*-cyclooctene with *tert*-butyl-hydroperoxide as oxidant. This complex reacted with water to form new complex [Mo_2O_6(Pent-pp)]. The [Mo_2O_6(Pent-pp)] complex was used as catalyst for epoxidation of bio-derived olefins DL-limonene (Lim) and the products were 1,2-epoxy-*p*-menth-8-ene and 1,2,8,9-diepoxy-*p*-menthane (yield 93 and 97%, respectively) [34].

Pyridine support non-nitrogen donor ligands. O-donor ligands supported by pyridine were synthesized by T.J. William and D. Schely in 2011 for oxidation of water. T.J. William carried out dehydrogenation of ammonia borane by very efficient ruthenium catalyst (**XXXXI**) for the production of two equivalent of H_2 (Scheme 10) [35].



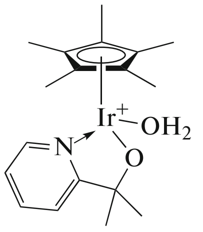
(XXXXI)



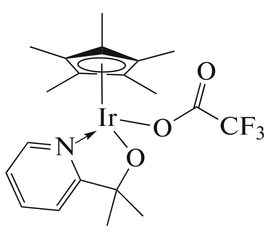
(Dehydrogenation of ammonia borane to produce hydrogen, borazine, and polyborazylene)

Scheme 10.

D. Schely with co-workers (2011) reported molecular iridium catalysts **XXXXII** and **XXXXIII**.



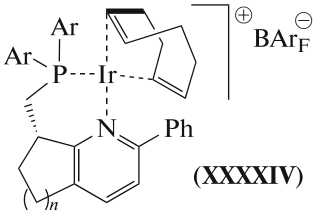
(XXXXII)



(XXXXIII)

Among them homogenous catalyst **XXXXIII** attracted the most attention because it was easily synthesized and characterized half sandwich complex. The homogenous **XXXXII** catalyzed water oxidation as identified by electrode mass with piezoelectric gravity. It involved oxygen during oxidation at electrode and did not form deposited material at electrode. The catalyst had wider application in artificial photosynthesis and solar energy storage and the key to electrochemical and photochemical systems capable of storing fuels [36].

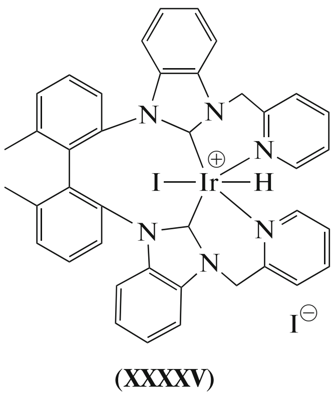
Andersson (2014) prepared phosphorous donor substituted pyridine ligands and their iridium complexes (**XXXXIV**) as a catalyst for hydrogenation of olefins.



(XXXXIV)

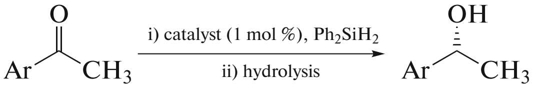
$n = 1, 2$

Generally olefins with three substituents were used and these substituents were either weakly coordinating or non-coordinating. These heterocyclic ligands were involved in tuning the reactivity of catalyst. The catalyst used was very reactive and enantioselective [37]. In 2013, Goufu and its co-workers prepared NHCs based Ir(III) complex (**XXXXV**) for the asymmetric hydrosilation of aryl methyl ketones.



(XXXXV)

NHCs ligand is important because of its air and moisture stability and strong sigma donor ability. This complex was stable in DMSO and acetone but insoluble in benzene and toluene. It possessed distorted octahedral geometry. It was prepared from the reaction of $[Ir(COD)]_2$, NaOAc, KI, and dibenzimidazolium salt. It showed the catalytic activity for the asymmetric hydrosilation of aryl methyl ketones yielding 1-arylethanol with moderate enantioslective excess value (Scheme 11). Enantioselective reaction was improved by lowering the temperature that increased the reaction time as more stable complex formed at lower temperature [38].

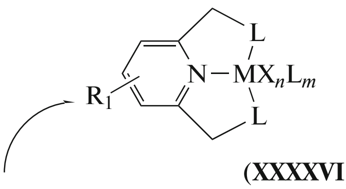


(Enantioselectivehydrosilationcatalyzed by Ir complex)

Scheme 11.

Pyridine Arms Supporting Same Ligand Functionalities

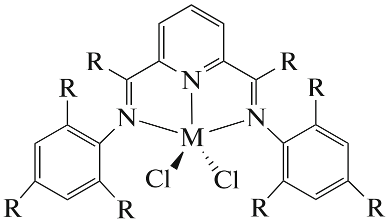
Transition metal complexes containing pyridine based pincer-type ligands have attracted increasing interest owing to the unusual properties of the metal centers imparted by the pincer ligand. Metal complexation with pincer ligands usually occurs with formation of two five-membered metallocycles to afford complexes $[MX_n(LNL)L_m]$ (**XXXXVI**), where X_n is counter anion, L is the pincer supporting arms and L_m is auxiliary ligand. These kinds of complexes have several sites that can be modified which will affect the properties of the metal center: the pendant ligands, the atoms connecting the extremes of the pincer with the aromatic ring, and the substituents on the aromatic ring [39].



(XXXXVI)

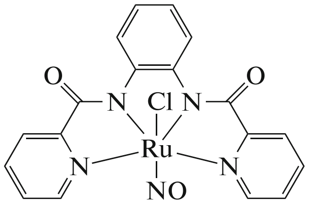
- Anchoring site
- Remote electronic modulations

Pyridine support same imine pendant arms. Gibson reported extremely active iron and cobalt based catalysts (**XXXXVII**) bearing 2,6-bis(imino)pyridyl ligands for the olefin polymerization [40].

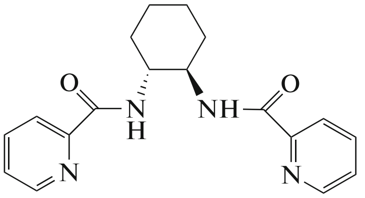


(XXXXVII)

Pyridine support same amidate pendant arms. C.F. Fortney developed the ruthenium nitrosyl compound (**XXXXVIII**) for use as nitric oxide delivery agents [41]. Trost synthesized the tungsten pyridine carboxamide complex (**XXXXIX**) to achieve high stereoselectivity in asymmetric catalysis [42, 43].

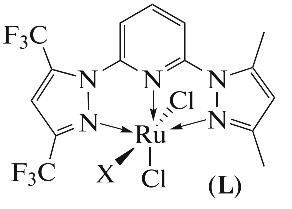


(XXXXVIII)



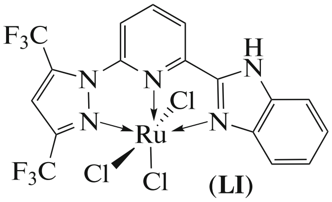
(XXXXIX)

Pyridine support same azole pendant arms. Yu (2014) synthesized the ruthenium complexes (**L**, **LI**) that contained pyrazolyl-pyridyl-based NNN ligands for the hydrogenation of ketones.



(L)

X = Cl: TOF ~ 5940 h^{-1}
X = PPh_3: TOF ~ 29700 h^{-1}

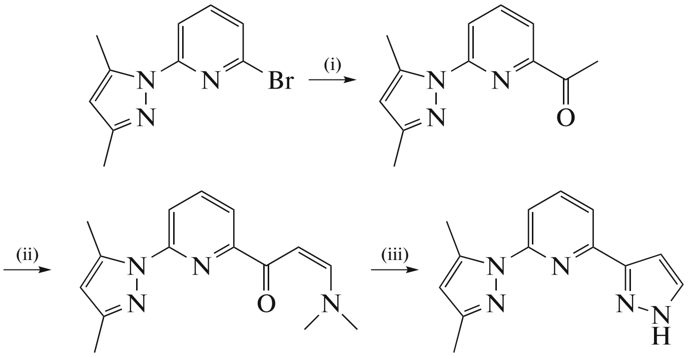


(LI)

Final TOF ~35640 h^{-1}

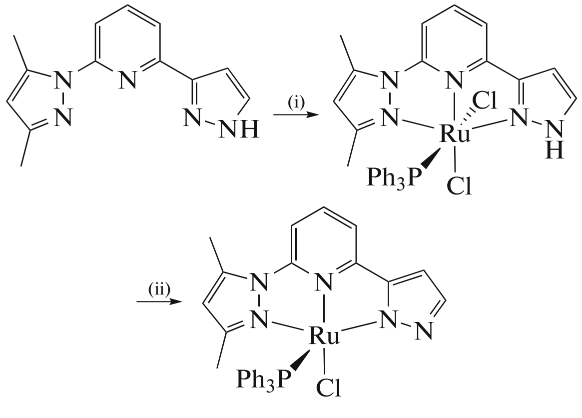
The benzimidazolyl functional group containing NH in the ligand increased the catalytic process of complex in the reduction of ketone as shown in **LI**. The reduction was carried out under the standard conditions. During the reaction, base PrOK was also used to start the catalytic process. Electronegative groups, first three halogens atoms increased the reaction rate. However the use of electron rich and sterically hindered substrate decreased the reaction rate [44].

Jin with co-workers (2012) prepared the unsymmetrical pyrazolyl-pyridyl-pyrazole ligand (Scheme 12) and their Ru(II) complexes (Scheme 13). These complexes exhibited high catalytic activity in transfer hydrogenation of ketone and achieving the TOF to 720000 h^{-1}. The catalytic reaction rate was enhanced due to presence of unsymmetrical NH group in the pyrazole arm [45].



(Synthesis of pyrazolyl-pyridyl-pyrazole ligand (i = *n*BuLi, –78°C, *N*,*N*-dimethylacetamide, Et_2O, 65%, ii = *N*,*N*-dimethylformamide dimethylacetyl, reflux, 14 h, 88%, iii = hydrazine hydrate, EtOH, reflux, 1.5 h, 82%))

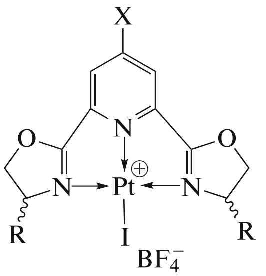
Scheme 12.



(Synthesis of Ru(II) complex (i = $RuCl_2$ (PPh_3), toluene, 110°C, 2 h, 85%, ii = K_2CO_3, CH_2Cl_2, room temperature, 10 h, 90%))

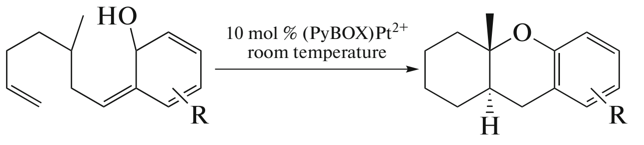
Scheme 13.

Nguyen (2014) studied (PyBOX)Pt^{2+} complex **LII** with square planner geometry.



R = *iso*-Pr, X = H (**LII**)

It was a chiral compound that involved in the cyclization of polyenes to polycyclic structure. The complex showed high diastereo-selectivity, moderate enantioselectivity and high yield product. The PyBOX ligand formed nitrogen donor bond with Pt^{2+}. The reaction of the (PyBOF)Pt^{2+} with the $AgBF_4$ was resulted in dication formation that reacted with polyene with the removal of one proton. Polar and non-coordinating solvent were required for cyclization. Generally, catalyst (PyBOX)Pt^{2+} coordinated with the less substituted substrate containing C=C bond. A proton was released and protodemetalation of N_3Pt-alkyle complex was also occurred. Polycyclic product was obtained (Scheme 14). Syringe pump was used due to possibility of side reaction. The reaction was carried out at room temperature. The product was separated by thin layer chromatography [46].

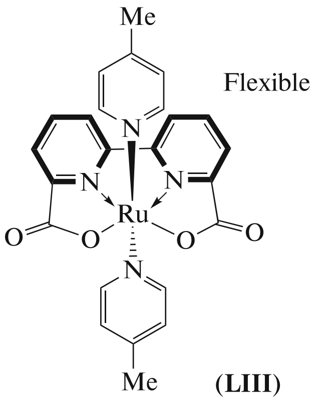


20 : 1 disteroselectivity
upto 93% yield

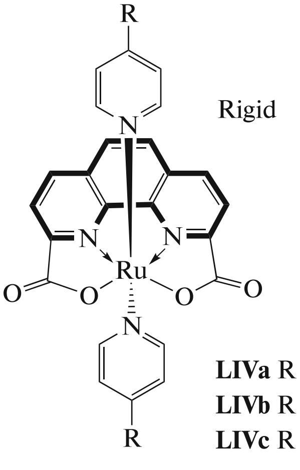
(Cyclization of polyenes with (PyBOX)Pt^{2+})

Scheme 14.

Pyridine support same O-donor ligand pendant arms. T. Privalov with co-workers (2011) used many Ru based complexes which were acted as a catalyst for the oxidation of water. The mechanism involved for the catalysis of water oxidation, like nucleophilic attack (WNA) took place by water molecule and direct coupling of O–O occur through the interactions of metals and oxygen molecules. They synthesized monomeric Ru complexes (**LIII**, **LIV**).



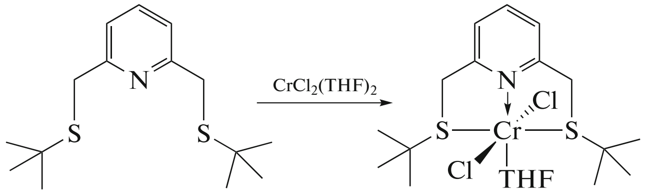
(**LIII**)



LIVa R = H
LIVb R = Me
LIVc R = Br

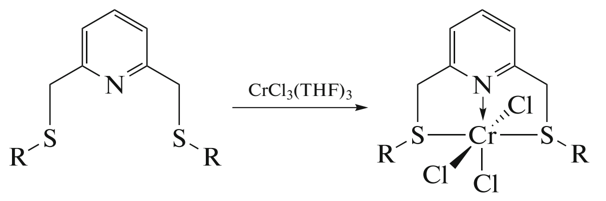
Small change in Ru bounded with ligands caused the oxidation of water from binuclear to mononuclear reaction. Complex **LIII** had important characteristics, elongated O–Ru–O bond, and provided the pathway for the solvent molecule to the middle of the Ru, stretchable back area provided the variety of oxidation states to Ru catalyst. They discovered that Ru complex had seven coordination number and two dimensional characteristics. Kinetic studies reported that at pH 1 water oxidation in the presence of catalyst **LIV** was second order. From X-ray crystallography, bond length of two oxygen molecules in catalyst **LIV** was smaller than in the catalyst **LIII** and the elongated O–Ru–O bond was longer than that in the catalyst **LIII**. Production of O_2 in homogenous catalysis by using catalyst **LIV (a–c)** were taken place in the presence of Ce because it acts as an oxidant. After several hours, they got good yield by using small amount of energy which was lower than that of catalyst. The phenomena of back bonding was occurred in these catalysts due to the donation of electrons from metal to ligands and protons were accepted by carboxylate ions. Ru(II) catalysts gave different colors to the complexes, long lasting transition states and multiple electron donating reactions [47].

Pyridine support same S-donor ligand pendant arms. K. Albahily with co-workers (2011) synthesized a self-activating catalyst containing chromium–SNS system. Two pyridine-SNS ligands (a and b) were synthesized and experimentally observed for the preparation of chromium trimerization catalyst, which worked actively and selectively. The divalent (Scheme 15) and two trivalent (Scheme 16) derivatives were isolated and characterized. When trivalent $[(2,6\text{-}CH_2SR)_2C_5H_5N]CrCl_3$ was treated with Me_3Al, a Chromium trimerization catalyst (Scheme 17) was obtained in crystalline form and was fully characterized. This catalyst was highly selective and self-activating. Highly pure 1-hexene could be produced without any further activation through this self-activating complex. Aluminate activators functioned as alkylating agent and Lewis acid. Neutral Me_2AlCl residue was dissociated with simultaneous transfer of alkyl group. Reductive elimination by two electron transfer resulted in the formation of monovalent and catalytically active specie [48].



(Synthesis of Cr(II) complex)

Scheme 15.

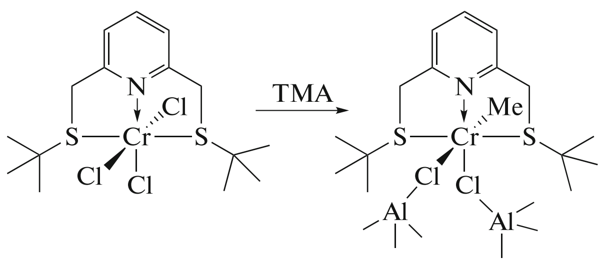


R = *t*-Bu (a)
n-decyl (b)

R = *t*-Bu (a)
n-decyl (b)

(Synthesis of Cr(III) complex)

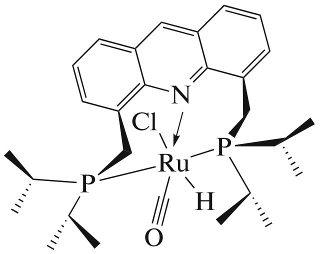
Scheme 16.



(Self-activating chromium trimerization catalyst)

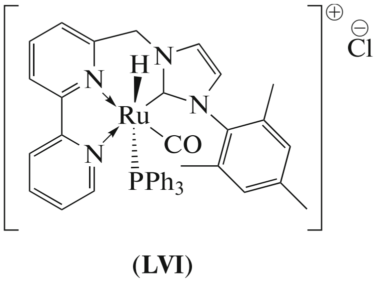
Scheme 17.

Acridine support same P-donor ligand pendant arms. Chidambaram with co-workers (2011) reported pincer type complex (**LV**) based on acridine which acted as a catalyst that leads to the activation of strong bonds, e.g. H–H, C–H (sp^2 and sp^3), O–H and N–H bonds and splitting of water. The functionality of catalyst involved reversible structure changes during substrate activation and formation of product. It was also used to catalyze the formation of primary amines from alcohol and ammonia [49].



(LV)

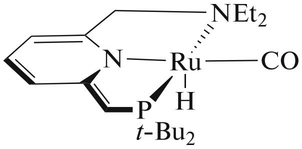
Bi-pyridine support NHC pendant arm. E. Fogler with co-workers (2011) synthesized new pincer ruthenium bipyridine N-heterocyclic carbene $[Ru(BPy)(NHC)(H)(CO)(PPh_3)]^+$ complex (**LVI**) for the catalytic hydrogenation of esters. The complexe was synthesized by the reaction of NHC ligand with $RuHCl(CO)(PPh_3)_3$. For hydrogenation one mmol solution of pentylpentanoate, catalyst (0.01 mmol solution) and KOtBu (0.01 mmol) in toluene were mixed and heated at 135°C under 5.4 atm of H_2. This complex is also catalytically efficient for the hydrogenation of non activated esters even under mild conditions [50].



(LVI)

Pyridine Arms Supporting Different Ligand Functionalities

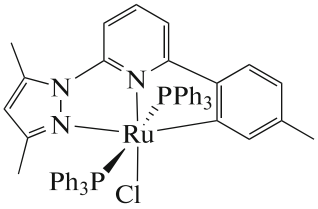
Extended aromatic pyridine support amine and phosphine pendant arms. G. Zeng with co-workers (2011) used the catalyst PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine)) Ru(II) hydride complex (**LVII**) for the reaction of alcohols with amines through dehydrogenation.



(LVII)

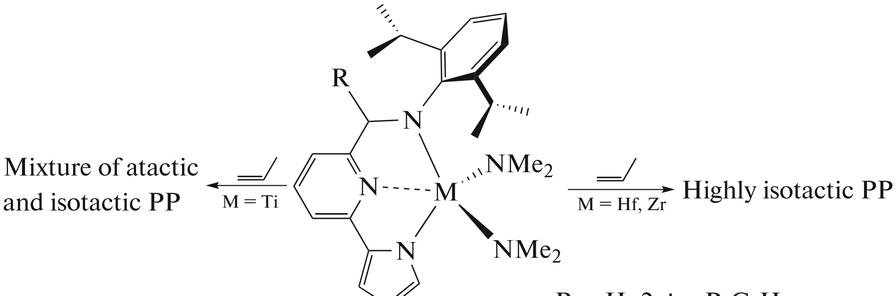
THE mechanism was facilitated by the metal ligand cooperation due to N-donor ability of the ligand. For the dehydrogenation purpose solutions were prepared in toluene and the reaction of alcohol and amine in the presence of catalyst was carried out under reflux. In the first step proton was transferred from hydroxyl of alcohol to the benzylic carbon of PNN ligand. Aldehyde was formed by the dehydrogenation of alcohol. In the next step aldehyde and amine combined to form hemiaminal intermediate through condensation reaction followed by a transfer of proton from the carbon of deprotonated substrate to the ruthenium center of PNN ligand. Finally Ru–H bond distance was increased and H_2 was eliminated from the dihydrogen complex [51].

Pyridine support phenyl and pyrazolyl pendant arms. D. Wangming with co-workers in 2012 presented a ruthenium(II)-NNC complex (**LVIII**) which act as a catalyst for the addition of ketones and oxidation of alcohols. This Ru-NNC complex showed very high catalytic activity due to irregularity around the metal [52].



(LVIII)

Pyridine support amido and pyrrole pendant arms. G. Li with co-workers synthesized four pyrrolylpyridylanilido [–NNN–] complexes with Ti(IV) and Hf(IV) (Scheme 18, R = H or i-PrC_6H_5) as a catalyst for ethylenes and propylenes polymerization. Catalytic activities of Ti catalyst having R = H was 1.0 and 3.9 for R = i-PrC_6H_5. Similarly Hf catalyst showed 0.4 and 0.9 catalytic activities for R = H and R = i-PrC_6H_5 respectively. Same ten minutes aging polymerization time was allowed at one atmosphere pressure at 25°C. In reaction of ethylene polymerization all these catalysts of Hf and Ti have approximately similar catalytic rate in the particular conditions while in case of propylenes polymerization all behave comparatively at different rates depending upon the symmetry of species, i.e., C_1-symmetric (Ti has more activity than Hf) or C_s-symmetric species (Ti has more activity than Hf). The symmetries, i.e., C_1-symmetry and C_s-symmetry vary by varing R group on bridged carbon. In these reactions a cocatalyst Al^iBu_2H/solid methylaluminoxane was used [53].



R = H, 2-*iso*-PrC_6H_4

+ Al^iBu_2H/MAO

Propylenes polymerization by early transition metal complexes containing pyridine supported amido and pyrrole ligands.

Scheme 18.

Thus, pyridine and its related ligands serve as a backbone for other pendant ligand functionalities. It can also serve as a bridge to bring together multiple functionalities at the same metal centre to tune the electronic properties of metal that is required to activate various homogenous catalytic reactions. Extended pyridine systems are very famous ligands to activate metal for oxidation of organic compounds and water.

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