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Development of Some Important Nitrogen Donor Ligands for Transition Metal Homogeneous Catalysis[1]

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Abstract—This review provides a broad overview of the literature related to the importance of ligands in homogeneous catalysis. In particular, it describes the types of nitrogen donor ligands that have typically been used for homogeneous catalysis. We surveyed the important transition metal homogenous catalysts explicitly from 2011 up to early 2014 and summarize their comparative catalytic activities. Generally, the main factors observed are the ligand structure, electron donor property and steric bulk which can affect the catalytic activity. Electron count and inductive effect can also influence the efficiency of homogeneous catalyst.

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INTRODUCTION

Catalysis is at the heart of chemistry as it provides tools for efficiently and selectively making and breaking chemical bonds, which are crucial for converting basic chemicals into useful products for society in a sustainable fashion [1]. Homogeneous catalysts, which generally consist of metal centres surrounded by a variety of ligands are highly versatile, act under mild conditions and can give very high selectivities. By varying the metal centre and the surrounding ligands, the chemo-, regio-, and stereo-selectivites can be tuned so that a very wide range of different products can be made available. As nature has served as a dominant source of inspiration in thearea of catalytic chemistry, it is no surprise that enzymes have served as natural prototypes for the design of catalysts. By far the oldest homogeneous catalysts are metalloenzymes, although one might wonder whether a metal complex built in to higher molecular weight proteins, encapsulated in a compartment of a cell is truly homogeneous. If the answer is positive it means the homogeneous catalysts are millions of years old. Some famous examples complexes are the following: iron porphyrin complexes active for oxidation, cobalt corrin (methylcobalamin) complex for carbon–carbon bond formation, copper imadazole (from histidine) complexes in hemocyanin, etc. [2].

To carry out a reaction with the help of homogenous catalyst, not only choice of metal is important but also the selection of ligand is equally important. Different transition metals are employed to carry out variety of organic reactions. Table 1 summarizes important homogeneous catalytic reactions and the metal catalysts that are used in industry [3]. Ligands play a key role in tuning the reactivity of metal complex. One metal can give a variety of products from one single substrate simply by changing the ligands around the metal center. For example, variety of products can be obtained from butadiene with various nickel catalysts. Polymers are obtained when allylnickel(II) complexes are used as catalysts and cyclic dimers and all the cyclic *trans* trimers are the products when Ni(0) is the catalyst precursor. Linear dimerisation requires the presence of protic species [4].

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. These properties of ligands can be explained in terms of steric and electronic properties. Modeling methods can be used to judge the steric properties of a ligand. However, electronic properties of a series of ligands are typically achieved using a spectroscopic probe, such as the IR vibrational frequency of a metal–CO complex, structural determination of M–L bond lengths (e.g., *trans*-influence) and reactivity studies. A comparison of electron donor strength of different ligands can be made by the carbonyl stretching frequency in a complex of type $Rh(L)(CO)_2Cl$. Lower the frequency higher would be

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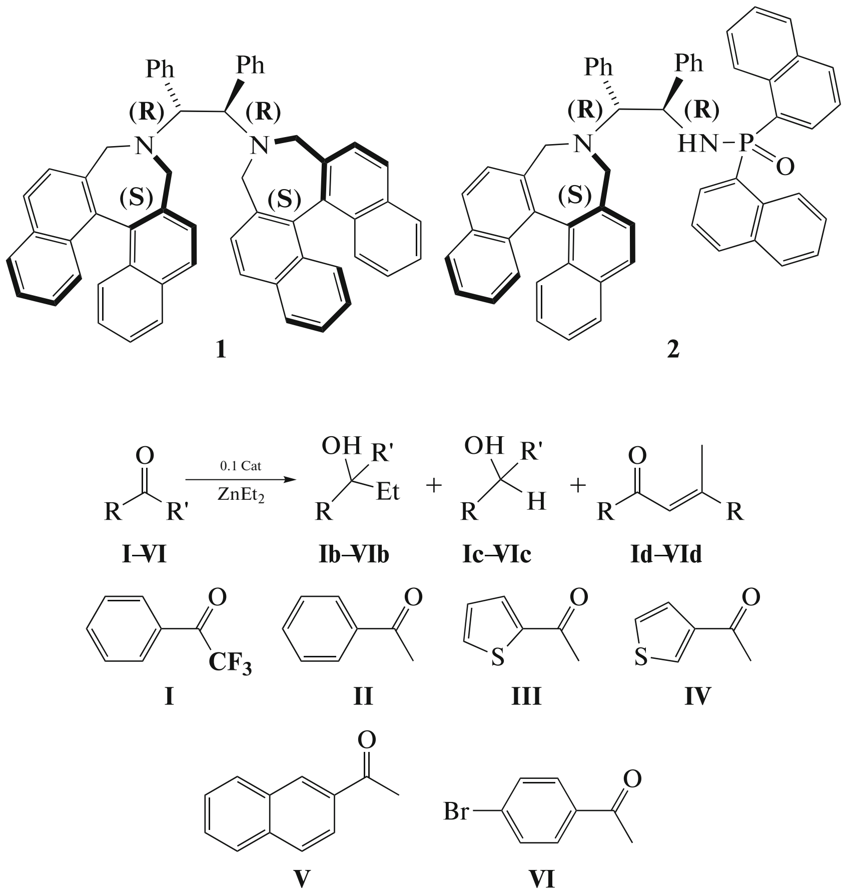
the electron donation by the ligand (L). However, structural determination of the M–L bond lengths (*trans*-influence) of ligands can be judged from comparison of X-ray data on palladium complexes containing a *trans*-(L)PdCl motif. Calculating above properties are useful for identifying metal–ligand combinations that give stable complexes and complex fragments that play a role in bond formation–cleavage processes, which could also potentially be catalytic. The role of ligand with respect to reactivity of metal complex can be judged by its contribution in increasing or decreasing metal catalyst activity in homogenous catalysis and in other stoichiometric reactions [5].

NITROGEN DONOR LIGAND COMPLEXES IN HOMOGENEOUS CATALYSIS

There are various types of nitrogen donor ligands that are used in homogeneous catalysis. Here we divided them in to six groups on the basis of their structure and ease of understanding.

Amines

Both symmetrical and unsymmetrical bidentate amines were used to activate metal catalysts. P. Espinet et al. reported that the addition of asymmetric organozinc, formed by combination of $ZnEt_2$ and **1** or **2** to chiral carbonyl compound yeilded chiral alcohol that occurs in natural compounds (Scheme 1, Table 2) [6]. In the same year, W. Baratta et al. studied that by adding ethylenediamine to NHC-phosphine ruthenium(II) complex yielded catalyst **3**. This can increase the rate and efficiency of catalytic transfer hydrogenation of ketone to alcohol in 2-propanol (Scheme 2) and achiving the TOFs up to 14000 h^{-1} [7].

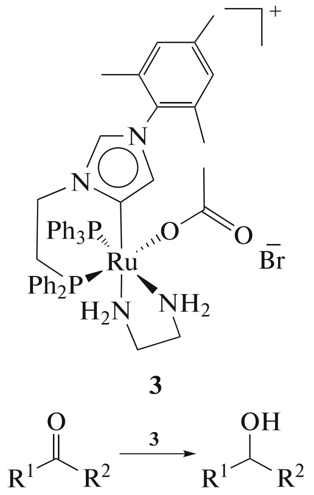


(Addition of $ZnEt_2$ to the aromatic ketones in the presence of 1 and 2)

Scheme 1.

Table 1. Important homogeneous catalytic reactions

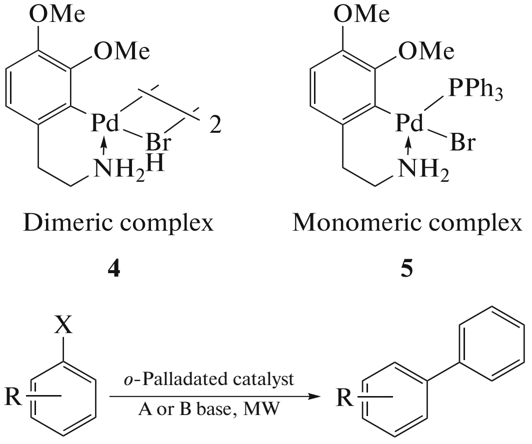
Common name	General metal catalyst	Common name	General metal catalyst
Carbonylation	Rh or Co	Water oxidation	Fe, Ru, Ir, Cu
Hydrocarboxylation	Rh, Pd, Co	Metathesis	Ru, Mo, Re
Hydroformylation	Rh or Co	Polymerization	Ti or Zr with Al; also Cr
Hydrocyanation	Ni	Oligomerization	Ni
Hydrosilylation	Pt	Auto-oxidation	Co, Mn and V
Hydrogenation	Rh or Co	Epoxidation	Mo
Asymmetric reactions	Rh, Ru, Ir, Cu, Ti, Mn, Co, Os, La, etc.	Wacker reaction	Pd and Cu



(Transfer hydrogenation of ketones to alcohols using catalyst 3)

Scheme 2.

A.R. Hajipour et al. carried out stille and hiyamma cross coupling reaction (SCC and HCC) with ortho-palladated complexes **4** and **5** containing primary amine (Scheme 3). The palladium used primary amine with pendant *o*-phenyl armto stabilise itself in catalyst. These moisture and air resistant catalysts can even couple non reactive aryl chlorides under microwave radiations (yields = 75% SCC, 70% HCC). For HCC, catalyst was much more efficient for aryl chlorides in the presence of base TBAF · $3H_2O$ (1.2 mmol), slightly polar solvent DMF, catalyst V (0.4 mol %) and at microwave 100°C and 600 W and for SCC, catalyst was much more active in the presence of K_2CO_3 (1.0 mmol), DMF, catalyst V (0.3 mol %) and at microwave 90°C and 500 W [8].



(A: $PhSn(Bu)_3$—stille reaction,
B: $PhSi(OEt)_3$—hiyama reaction)

Scheme 3.

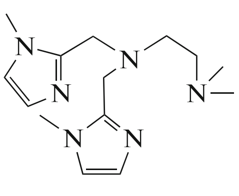
Table 2. Results of the addition of $ZnEt_2$ to the aromatic ketones in Scheme 1 with 1 and 2

Entry	Ket	L	Addition nb (ee %, conf.)	Reduction na	Self-aldol nb	Starting material n
1	1	2		100		
2	1	1	97 (92)			3
3	2	2	52 (87, R)[a]		45	3
4	2	1	3	14	62	21
5	2			69	21	10
6	3	2	19 (91)	45	30	6
7	4	2	56 (92)	25	18	1
8	5	2	58	26	15	1
9	6	2	27 (93)	22	46	5

[a] The absolute stereochemistry for 2b was determine by comparing with literature data.

[b] The self-aldol products are in fact a mixture of the α,β-unsaturated ketone and the hydrate derivative.

The extended arm of amines like pyrrole, azole and phenolate can also aid metals in homogenous catalysis. Balamurugan and its co-workers carried out oxidation of alkanes in the presence of *m*-chlorobenzoic acid (*m*-CPBA) used as oxidant. They synthesized $[Ni(L)(CH_3CN)_2](BPh_4)_2$ complexes where L is amine based complexes (**6**, **7**) as catalysts for these reactions. In oxidation of adamantane, ethylbenzene and cumene, the catalyst with 6 gave yield of 50.4, 33.3, and 28% with turnover numbers (TON) 504, 333 and 280, respectively, and the catalyst complex with 7 gave yield of 39.8, 28.4, and 26.8% with TON 398, 284, and 268, respectively [9]. Donnelly explored amine with three pendant triazole groups to prepared the copper tris(triazolylmethyl)amine catalyst **8** for "click" cycloaddition reactions [10]. It was synthesized by the reaction of copper chloride with TBTA in acetonitrile. Goldschmidt prepared the ultra-highly active non-metallocene catalysts **9**, **10** that feature an amine bis(phenolate) ligand for polymerization of α-olefin monomers [11].



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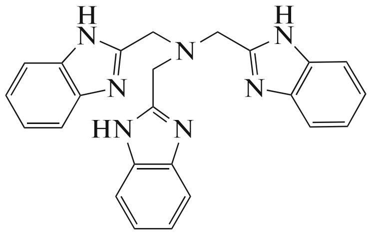

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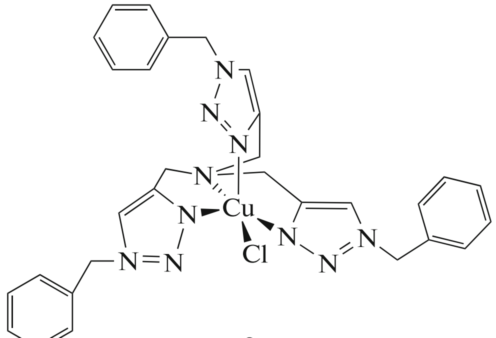

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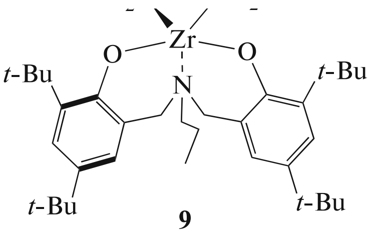

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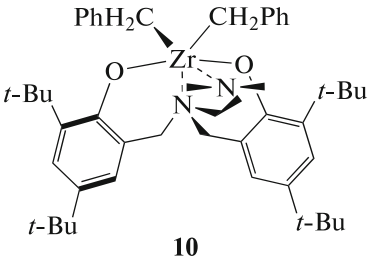

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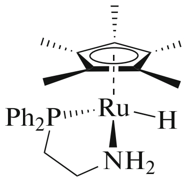
Amine complexes stabilised with phosphines or carbenes pendant arms were used to increase electron donor property at the metal center. Muniz prepared the ruthenium-amine catalysts **11–14** with phosphorous donor ligand arms for the hydrogenolysis of epoxides and for the conversion of diols to lactones and some ruthenium-amine bifunctional metal–ligand catalysts for the isomerization of allylic alcohols and the reduction of polarized C=C bonds [12]. Similarly, in 2013, Chen and Zhang synthesized *trans* octahedral diphosphinediammine ruthenium complex (**15**). This complex showed high degree of enantioselectivity up to 99.9% ee due to synergestic effect of nitrogen containing ligand and hydrogenated product obtained 77% ee. In second ligand, chiral amminophosphine form complex with iridium has octahedral geometry (**16**). These nitrogen containing ligands catalysed the hydrogenation of ketones under homogenous phase during which secondary alcohol formed that acts as intermediate for wide rang of applications in pharmaceutical and advance materials [13]. In 2012, W.N. Wylie et al. studied ruthenium precatalyst (**17**) for the hydrogenation of ketone to an alcohol and proposedouter sphere bifunctional mechanism. They found out that phosphine replaced by NHC resulted in more efficient catalyst [14].



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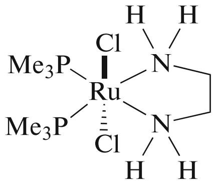

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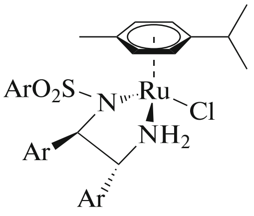

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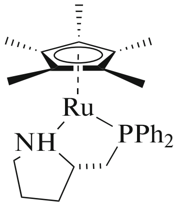

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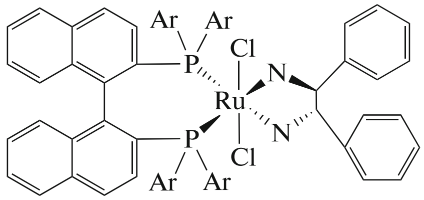

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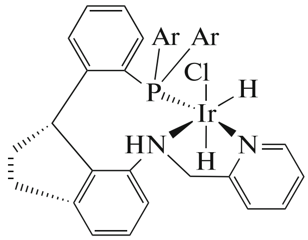

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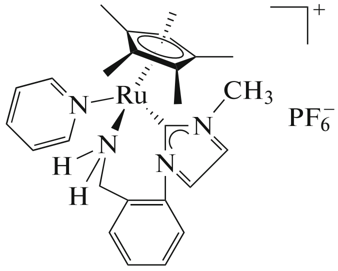

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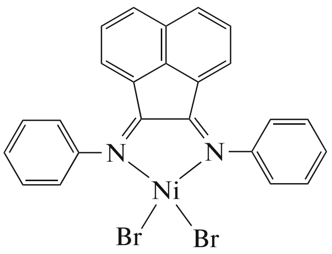
Imines and Related Ligands

In this class, we discuss metal complexes with C=N in the ring containing metal (imine, oxime, hydrazone and thiosemicarbazone ligands) and iminophospharane.

Imines. Nickel and palladium imine complexes have been reported by Brookhart (**18**) [15] and Sun (**19**) [16]. They showed good activity and selectivity for oligomerization and polymerization of ethylene. In 2013, Masdeu-Bultó and its coworkers stabilised chromium with extended amido groups (**20**) for the cyclic addition of CO_2 into styrene oxide that gave the cyclic styrene carbonates in 68% yield (Scheme 4). Other terminal epoxides like propylene oxide, 1,2-epoxidehexane, 1,2-epoxidetetreadecane, epichlorydrin can be obtained by the same catalyst system (0.2 mol %) in high yield around 58–95% in 30 min [17].



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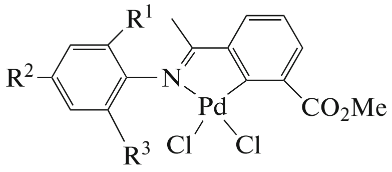

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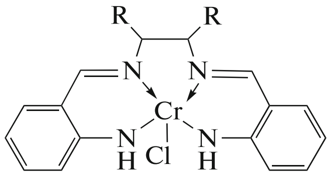

R, R = $-CH_2-CH_2-$

or R = R = H

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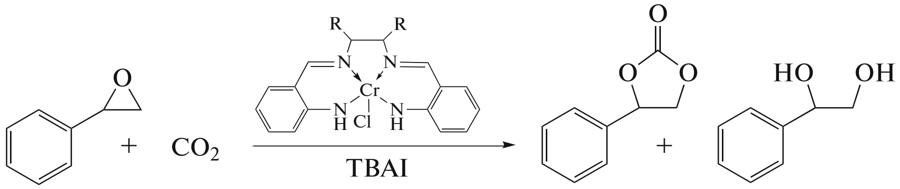
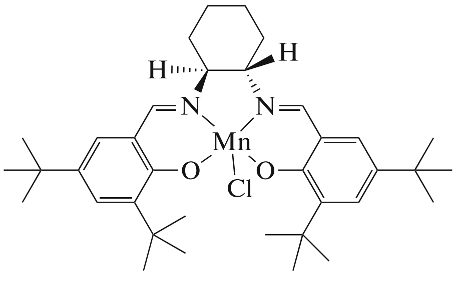


Scheme 4.

Imine complexes stabilised with pendant O-donor ligand are common homogeneous catalysts. Jacobsen [18, 19] and Katsuki [20] independently prepared imine based metal complexes for asymmetric epoxidation. They used chiral derivatives of the $[Mn(Salen)]^+$ complexes and oxidants, such as PhIO and NaOCl (commercial bleach) under phase-transfer conditions to achieve the catalytic epoxidation of simple olefins with enantiomeric excesses exceeding 90%. Some examples are **21** and **22**. Chirality was introduced in the essentially planar salen-manganese system by replacing the ethylenediamine backbone by optically active 1,2-diphenylethylene diamine or *trans*-1,2-diaminocylohexane. Furthermore, it was crucial that the ligand bears bulky substituents adjacent to the phenoxy oxygen atoms. Whereas Jacobsen showed that a *tert*-butyl group adjacent to the phenoxy oxygen atoms was sufficient to achieve high selectivities in the phase-transfer process (using NaOCl as oxidant), Katsuki obtained better results (with PhIO as oxidant) by introducing a stereogenic 1-phenylprop-1-yl group. Dong (2014) prepared a distorted octahedron cobalt complex (Scheme 5) by reacting a tridentate schiff base with cobalt acetate. It was used as a catalyst for the synthesis of polybutadiene. This catalyst supported the polymerization of 1,3-butadiene into *cis*-1,4-polybutadiene on a large industrial scale at about 70°C temperature. The activity, regio-stereo selectivity and polymer properties of the product were also controlled by the catalyst. Yield of the product was 94–98% [21]. Jin-GuoXin found out that the activated by methylaluminoxane, mononuclear bis(hydroxyindanone-iminate)nickel complexes $Ni[ArN{=}CC_2H_3(CH_3)C_6H_2(R)O]_2$ (Ar = 2,6-*iso*-$Pr_2C_6H_3$, R = Me, Cl, and H) **23** showed good activity for the styrene polymerization [22]. The effect of many reaction parameters including the Al/Ni ratio, temperature, and reaction time on catalytic activities of catalytic systems and the molecular weights of the obtained polystyrene was ascertained. The highest activity (1.34×10^5 g(PS) mol^{-1}(Ni) h^{-1}) was obtained under the optimum reaction conditions. The ^{13}C NMR spectra of the polymers revealed that the polymer was isotactic-rich atactic polystyrene. The coordination mechanism was confirmed by the analysis of the polymer chain end-groups.



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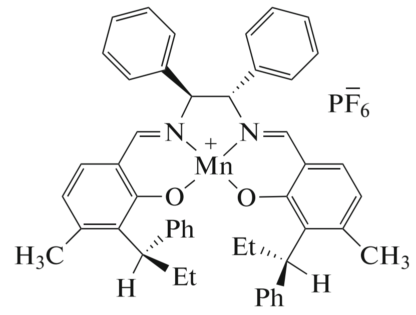

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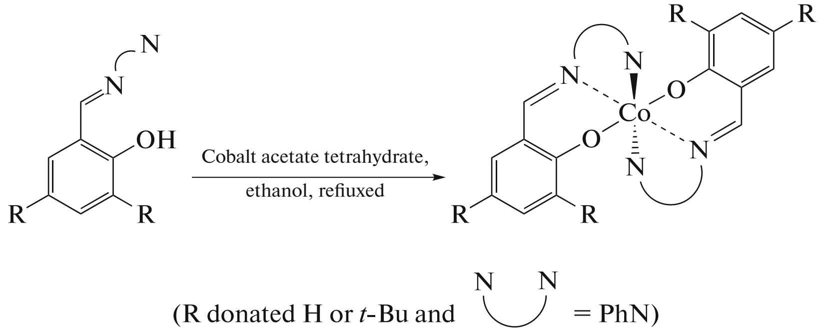
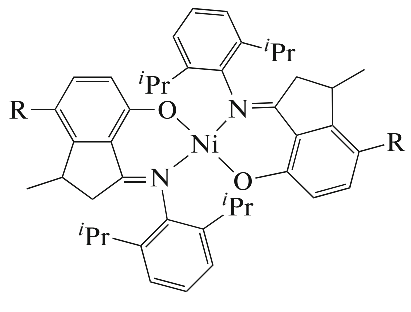


(R donated H or *t*-Bu and = PhN)

Scheme 5.



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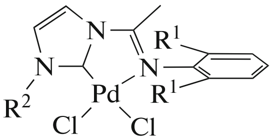
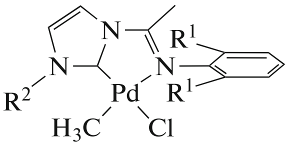
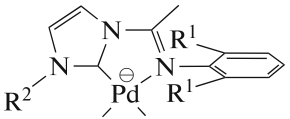
Gao and Wu studied structures and catalytic activities of bidenate imine and N-heterocyclic carbene containing palladium complexes. They found out that **25** and **26** with square planar geometry however palladium dichloride complex (**24**) showed distorted square planer geometry. In these three complexes, cationic palladium complex (**XXV** and **XXVI**) showed best catalytic properties towards polymerization of norbornene. Cationic palladium complex proceeded via coordination insertion mechanism [23].



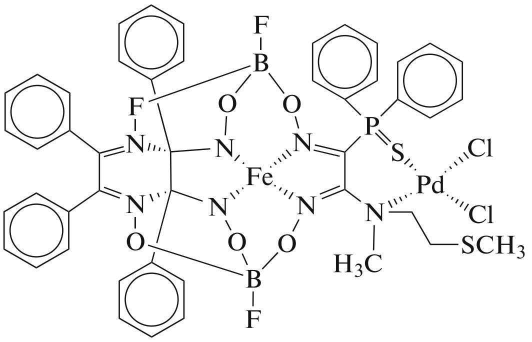




$R^1 = R^2 = CH_3$

24 **25** **26**

Oxime. Voloshin prepared monophosphorylated cage complex (**27**) by the nucleophilic substitution of iron(II) dichloroclathrochelate and diphenylphosphinesulfide followed by nucleophilic substitution with mono and diamines. These P,N-substituted mono and bis-clathrochelates were used as N,S-donor macrocyclic ligands for palladium ion. The complex was thermodynamically favourable, and its stability was attributed to the large donating capability of the nitrogen atom and disposition of its donating sites. In this complex Pd and Fe are in 1 : 1 and showed the distorted octahedron geometry as it is low spin Fe(II) complex. It was used as a catalyst for suzuki cross-coupling reaction of iodobenzene with phenylboronic acid in DMF at 100°C using K_3PO_4 as base for about 4 h. It gave the maximum yield for C_6H_5I (99%) and 78% for C_6H_5Br [24]. Vincent reported a new family ofcobalt and nickel dioxime di-imine complexes (**28**, **29**) as efficient and stable molecular electrocatalystsfor hydrogen evolution at low voltages [25]. These platinum free complexes increase the economic viability of hydrogen production. The hydrogen was evolved from acidic nonaqueous solutions, and a mechanistic study showed that the reaction went through bimetallic homolytic pathway. The presence of a proton-exchanging site in the ligand, provided an exquisite mechanism for tuning the electrocatalytic potential for hydrogen evolution of these compounds in response to variations of the acidity of the solution, a feature only reported for native hydrogenase enzymes so far.



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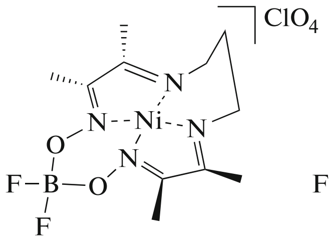

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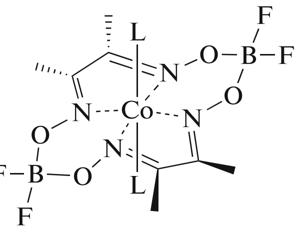

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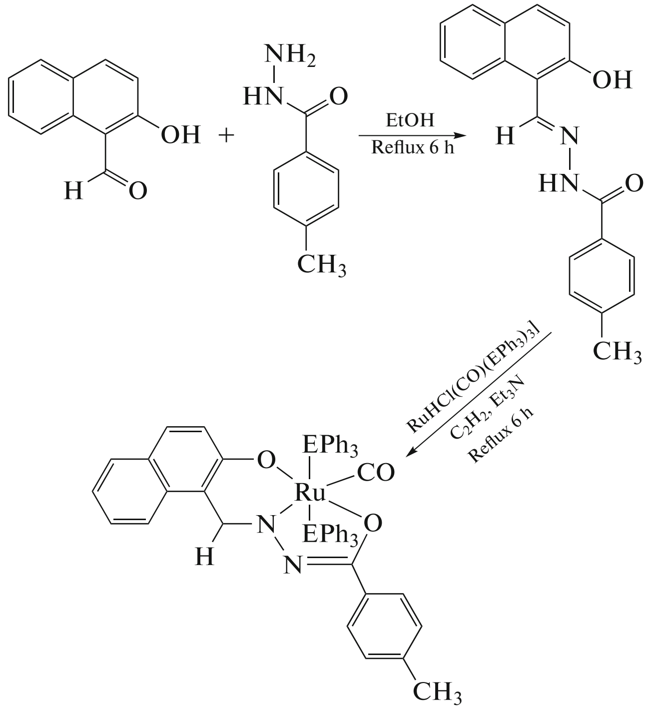
Hydrazone and thiosemicarbazone. R. Ramesh synthesized eight new octahedral complexes by reaction of $[Ru(HCl)(CO)(EPh_3)_3]$ and substituted benzoylhydrazone ligands (Scheme 6). The general molecular formula of complexes was $[Ru(L)(CO)(EPh_3)_2]$, where H_2L = 2-hydroxy-1-naphthaldehyde benzoylhydrazone ligands; E = P or As. These complexes acted as effective homogeneous catalysts for the transfer hydrogenation reactions of ketones giving secondary alcohols with up to 99.5% conversion. The composition of complexes was revealed by elemental analysis and spectral methods. X-ray diffraction analysis showed the distorted octahedral structure. Ligands were attached to the central metal atom through phenolate oxygen, azomethisne nitrogen and imidolate oxygen. The complexes showed a quasi-reversible reduction and two reversible oxidations. The product formation is influenced by nature of base, temperature, catalyst loading and reaction time [26]. In the same year, N. Rupesh and its coworkers worked on square planar binuclear Pd(II)-terepthaldehydebis(thiosemicarbazone) complex (**30**), that acted as a catalyst for Mizoroki-Heck reaction of 4-chloroacetophenone with olefins (Scheme 7, Table 3) [27].

Table 3. Mizoroki-Heck reaction of 4-chloroacetophenone with olefins

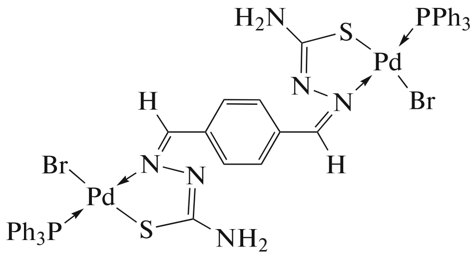
Entry	R^1	Yield, %[a]	TON[b]	TOF[c]
1	$-COO^tBu$	44	440	18.3
2	$-COOCH_3$	46	460	19.2
3	$-C_6H_5$	35	350	14.6
4	$-C_6H_4$-4-CH_3	30	300	12.5
5	$-C_6H_4$-4-Cl	38	380	15.6

[a] Isolated yield after column chromatography based on 4-chloroacetophenone(average of two runs).
[b] TON (turnover number) = ratio of moles of product formed to moles of catalyst used.
[c] TOF (turnover frequency) = TON per hour.



(Formation of ruthenium(II) carbonyl benzoylhydrazone complex (E = P or As))

Scheme 6.



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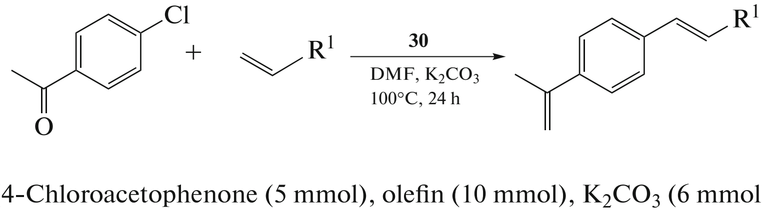
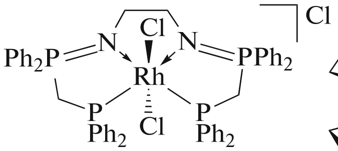


(4-Chloroacetophenone (5 mmol), olefin (10 mmol), K_2CO_3 (6 mmol), complex 30 (0.1 mol %), DMF (3 mL), N_2 atmosphere; various R^1 used are mensioned in Table 3)

Scheme 7.

Iminophosphorane. V. Cadiemo reported the use of tetradentate iminophosphorane ligand with pendant phosphine arms containing rhodium complex **(31)** as catalyst in the hydrogenation reaction of acetophenone derivatives in 96–99% yield at 82°C in 8–18 h. Complexes of these type of ligand were also used as a catalyst for oxidation reactions, allylic alkylation, oligomerization, cyclopropanation, cross coupling and hydrogenation reactions. He also synthesized iminophosphorane-phosphines based ferrocenyl complex $[Rh(Nbd)_2[BF_4][Ir(Nbd)_2[BF_4]$ (**32**) from rhodium(I) and iridium(I) precursors $[M(Cod)_2][BF_3]$ (M = Rh, Ir). These complexes acted as a catalyst for asymmetric hydrogenation of unfunctionalized di-, tri- and tetrasubstituted olefins [28]. Grevy (2014) reported the synthesis of iminophosphorane supported by phenyl and sulphur donor ligands $(Ph_3P{=}NC_6H_4SR)$ (R = CH_3, C_6H_5). These tridentate ligands with $[Na_2PdCl_4]$ formed iminophorane pincer complexes $[PdCl\{C_6H_4(Ph_2P{=}NC_6H_4SR\text{-}k^3\text{-}C,N,S)\}]$ (R = CH_3, C_6H_5) (**33**) which possessed extraordinary reactivity and catalytic activities in homogeneous catalysis. Pincer complexes of this type were used as catalysts for suzuki-miyaura cross coupling reactions of para-substituted bromobenzenes, C–H bond activation and polymerization of ethylene [29].



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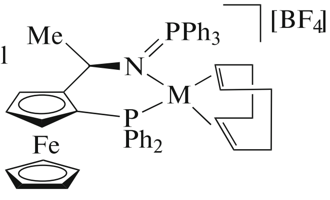
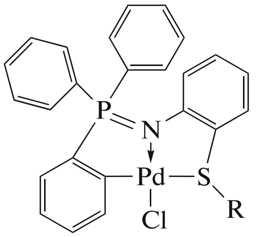


M = Rh, Ir

32



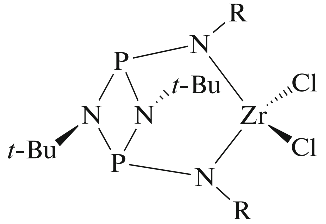
R = CH_3, C_6H_5

33

Amido and Amidate Related Ligands

In this class, we discuss those metal complexes in which there is negative charge on the nitrogen in M–N like amido, amide and amidate ligands. It also includes those in which pyridinium moiety is introduced to over all neutralize any negative charge on the nitrogen in M–N like pyridinium amide and pyridiniumamidate ligands

Amido/amide. Amido complexes of zirconium were prepared by Repo (**34**) for ethene polymerization [30]. He found that the catalytic behavior was dependent on the bulk of the ligand substituents. The nature and size of amido substituents played a great role in defining the catalytic activity of the complexes and polymer properties. Klosin synthesized hafnium and zirconium imino-amido complexes (Scheme 8) from bis-imine ligands, and these resulted in a new family of olefin polymerization catalysts [31]. He found that the hafnium imino-amido complex was best followed by hafnium diamido complex. In 2012, J. McNulty synthesized silver complex (Scheme 9) as a solvate free, air stable compound. It is soluble in many organic solvents and form clear solution, unaffected for weeks through heating/cooling cycles and no precipitation of silver metal is observed. He also used this complex for silver mediated azide-alkyne cycloaddition (AAC) reaction [32]. A. Chartoire et al. (2011) synthesized bidentateamido-phenyl palladium complex (**35**). It showed high catalytic activity in buchwald-hartwing reaction, allowed coupling of different hetero-arylchloride, over a variety of amines with high yield (72–97%). This complex overcomes the challenge of coupling inactivated chlorides at low catalytic loadings. Bulkiness of amines determined the amount of palladium used [33].



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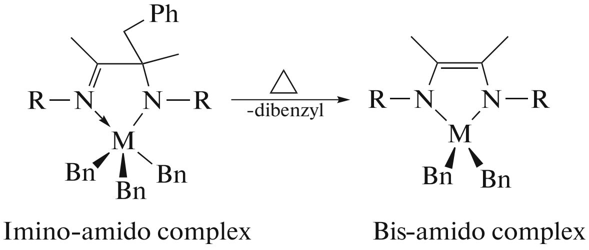
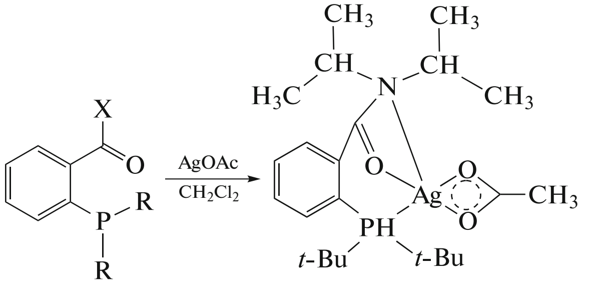


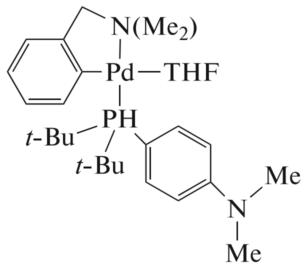
M = Hf, Zr; R = 2,6-*iso*-$Pr_2C_6H_3$

Scheme 8.



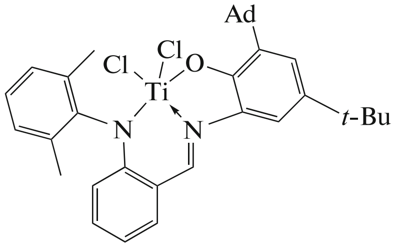
R = *t*-Bu, X = $N(Ipr)_2$, where $N(Ipr)_2$ is N-isopropyl

Scheme 9.



35

Gao and Mu synthesized amido based titanium complex (**36**) chelated by phenoxy and imine tridentate ligand with geometry resided between square pyramid and trigonal bipyramid. It can act as a precatalyst for ethylene polymerization at 70°C in the presence of toluene. In such complex, substituents on the amido nitrogen was closed to the metal center that provided a bulkier coordination environment around a metal center and hence greatly affected the catalytic performance of complex. The complex bearing adamantly substituted ligand showed greater catalytic activity for ethylene polymerization. Catalytic activity became higher by increasing the size of 2,6-R_2Ar group at amide N atom. The reason was that bulky substiuents on the ligand shielded the metal center and thus, prevented catalytically activated species from deactivation. Catalytic activity was also increased with increase in Al/Ti ratio from 50–100 which was at 100 in case of 3*d* complex and with the increase in polymer temperature from 70–100°C which was 70°C in case of 3*d* complex and yield was 0.28 g [34]. Lippard et al. have shown that chiral aminotroponeiminates (**37**) were effective ligands in Cu-catalysed conjugate addition of Grignard reagents to cyclohexenone [35]. This virtually unique ligand system afforded enantiomeric excesses as high as 74%. Breitenfeld et al. synthesized the amidonickel(II) hydride complex stabilised by two amine pendant arms (Scheme 10). It was found out that it could decompose in solution at room temperature via two pathways. In the first pathway, the complex decomposed to give protonated ligand ($^{Me}N_2NH$) and the black metallic precipitate, and N–H reductive elimination occurred. In the second pathway, the complex was decomposed due to intermolecular reaction with H_2, 5-coordinated nickel(II) complex and nickel particles as the products. The N–H reductive elimination is faster than intermolecular process as N–H reductive elimination is intramolecular process. This decomposition was avoided by conducting this reaction at –70°C. Nickel hydride complexes are inserted into double bond (C=C) and (C=O) [36].



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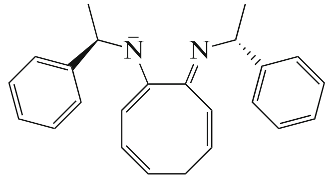

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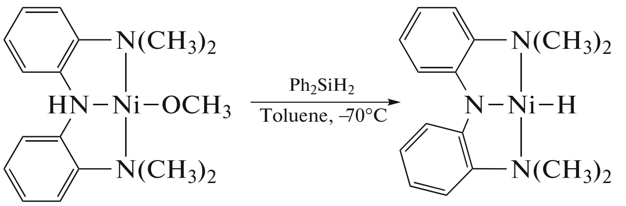
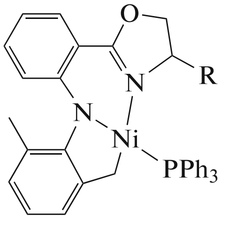


Scheme 10.

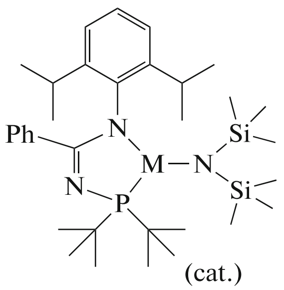
L.Z. Lu et al. synthesized chiral amido pincer CNN nickel complexes stabilised with oxazoline and benzyl pendant arm through activation of carbon hydrogen bond of β-diketiminato ligands (2-(2'-R^1NH)-phenyl-4-R^2-oxazoline) react with *trans*-$NiCl(Ph)(PPh_3)_2$. Mono and dinuclear Ni complexes were formed with nickel sources like $Ni(OAc)_2$, $Ni(Acac)_2$, $NiBr_2$, $NiCl_2(Py)_4$, and $NiCl_2$ treated with ligand. If *trans*-$NiCl(Ph)(PPh_3)_2$ was used as main source then $(NN)NiI(PPh_3)$ was obtained. The same product was obtained by the addition of β-diketiminato ligand which caused reduction of Ni(II) to Ni(I) complexes. If bulky ligands like ketiminato and salicylaldiminato were treated by *trans*-$NiCl(Ph)(PPh_3)_2$, then Ni(II) complexes (**38**) were formed. It was paramagnetic and square planner. The stabilization was enhanced by C–M bond along with two adjacent arms from other ligands. Resulting compounds were sensitive to air and had low yield and by the addition of $C_{38}H_{37}N_2NiOP$ in these compounds, the yield increased to 35%. These compounds were proved active catalysts for hydroamination, dehydrogenation and C–C coupling reactions [37].



R = Ph

38

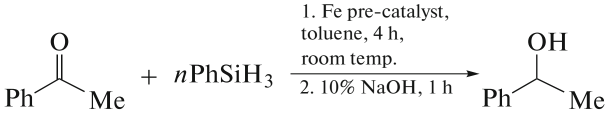
L. Sydora et al. studied mixed bidentateamido and phosphine known as N-phosphinoaminidate ligand and its complexes with iron(II) and cobalt(II) (**39**). Both of them acted as precatalyst for the hydrosilylation of carbonyl compounds like ketone, aldehyde and esters (Scheme 11). High electron donor ligands increased the electronic density around metal center that in turn increases the activity of metal centre towards reduction of aldehydes, ketones and even for esters at remarkably low loadings (0.01–1.0 mol % Fe) and used only 1 equivalent of phenylsilanereductant ($PhSiH_3$, Ph_2SiH_2 or $PhMeSiH_2$) [38]. Abdur Rashid and co-workers synthesized iridium complex of mixed tridentate amido ligand with two trialkylphosphine arms as air stable iridium chlorodihydride $IrH_2Cl[(iso\text{-}Pr_2PC_2H_4)_2NH]$. It was prepared by the reaction of $[IrCl(COE)_2]_2$ with the pincer ligand ($iso\text{-}Pr_2PC_2H_4)_2NH$ in 2-propanol at 80°C followed by reaction with KO^{t}Bu in THF resulted in the formation of the air-sensitive amidodihydride complex $IrH_2[(iso\text{-}Pr_2PC_2H_4)_2N]$. This reaction proceeds in the presence of 2-propanol that readily forms the moderately air-stable trihydride complex $IrH_3[(iso\text{-}Pr_2PC_2H_4)_2NH]$ (Scheme 12). The trihydride and amidodihydride complexes in the absence of a base are exceptionally active catalysts for the transfer hydrogenation of ketones in 2-propanol [39].



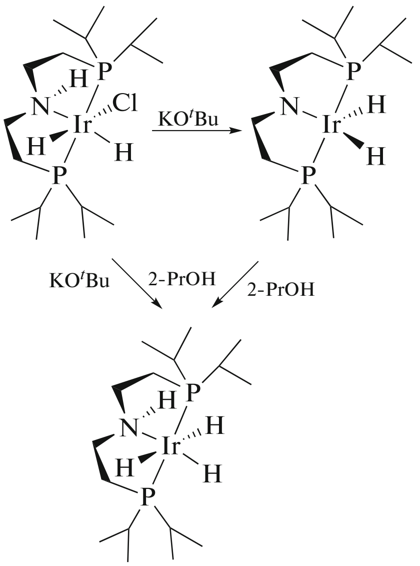
(cat.)

M = Fe, Co

39



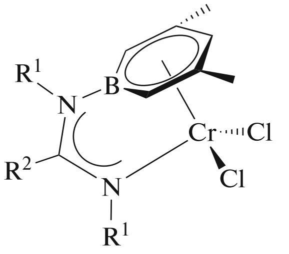
Scheme 11.



(Rashid hydrogenation transfer hydrogenation catalysts for ketones)

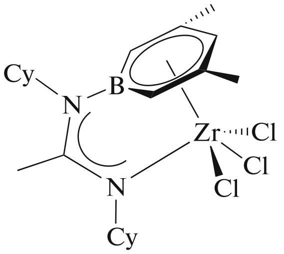
Scheme 12.

Chen reported the synthesis of boratabenzene complexes with zirconium and chromium (**40, 41**). They showed excellent catalytic activity for the transformations like olefin polymerization, hydroamination and hydrosilation. Chromium complexes with MMAO used as a co-catalyst exhibit excellent catalytic activity for ethylene polymerization and produce high molecular weight polymers. Temperature can effect the production like at 30°C it was 88.5 and at 70°C it was 170.0. These metal complexes also catalyse olefin co-polymerization. Ligand environment also effected the catalytic activity like chromium dichloride complex catalytically was active as mensioned before while zirconium dichloride complex was catalytically inactive [40].



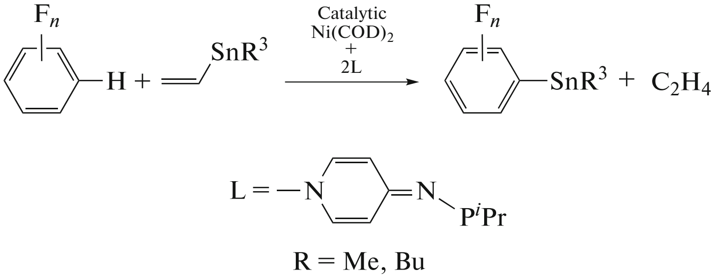
$R^1 = iso\text{-}Pr$, $R^2 = Me$

40



41

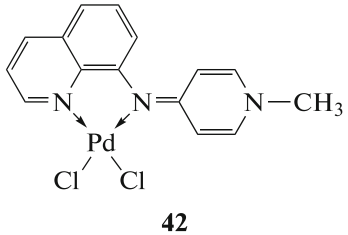
Pyridinium amide (PYEs). Johnson tested for the first time the ability of the pyridinium amide ligands to aid in the oxidative addition of challenging substrates. For example, he studied activation of the strong and relatively inert C–F bonds in fluorinated aromatics by generating in situ nickel(0) PYE complexes [41]. In 2010, he was successful in catalytic C–H bond stannylation [42]. This is absolutely a new regioselective pathway to C–Sn bonds via C–H bond functionalization using an in situ generated nickel PYE complex as a catalyst. It could have significant impact as a facile route to reagents for the Stille coupling reactions, which are widely utilized because of the air and moisture stability and functional group tolerance of the organotin compounds. The syntheses of these organotin reagents typically involve multiple steps from expensive functional-group-containing precursors. He found that upon addition of $H_2C{=}CHSnBu_3$ and a partially fluorinated arene to catalytic amounts of $Ni(COD)_2$, and $MeNC_5H_4N$-*iso*-Pr at room temperature yielded no C–F activation products but practically quantitative catalytic conversions to the products of C–H functionalization, $C_6F_nH_{5-n}SnBu_3$ (Scheme 13). The stoichiometric production of ethylene as a byproduct was positively identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy when the reaction was performed in C_6D_6 in a sealed NMR tube. The reaction was found to go to completion with as little as 1 mol % $Ni(COD)_2$ and $MeNC_5H_4N$-*iso*-Pr and provided a practically pure product, as monitored by ^{19}F, ^1H, and ^{119}Sn NMR spectroscopy.



(General reaction scheme for the catalytic stannylation of C–H bonds)

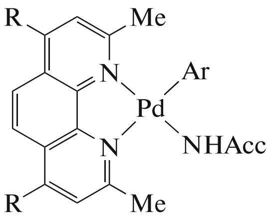
Scheme 13.

In 2011, we synthesized pyridinium amide based palladium complex, $[Pd(PYE)Cl_2]$, (**42**) [43] from 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 [43].



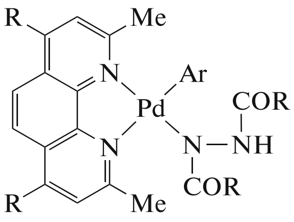
42

Amidate. Muniz successfully worked on catalytic aryl-nitrogen bond formation from palladium amidate complexes (**43–45**) that bear phenanthroline-type ligands [44]. Palladadiaziridine acted as key intermediate in this catalytic homogeneous reduction of azo compounds. In 2013, Luis reported a polymer supported α-amino amidate ligand (**46**), synthesized from natural amino acid. An inactive homogeneous system was converted into an efficient catalyst by using its zinc complex (**47**) towards enantioselective addition of diethylzinc to aldehyde that result into optically active secondary alcohol, and enantioselectivity up to 95% obtained. The catalyst is reusable without loss of catalytic activity [45].



Aryl-palladium amidate
(Acc = Tos, COR, COOR, NCOOR)

43



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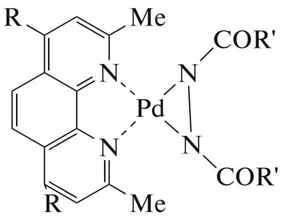
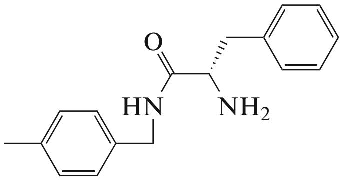


R = Ph, R' = OEt, O-*iso*-Pr,
O-*t*-Bu, OBn

45



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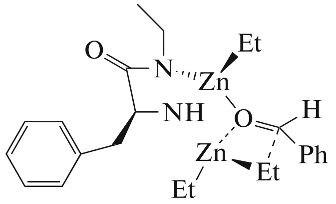
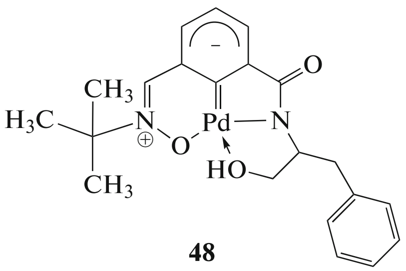


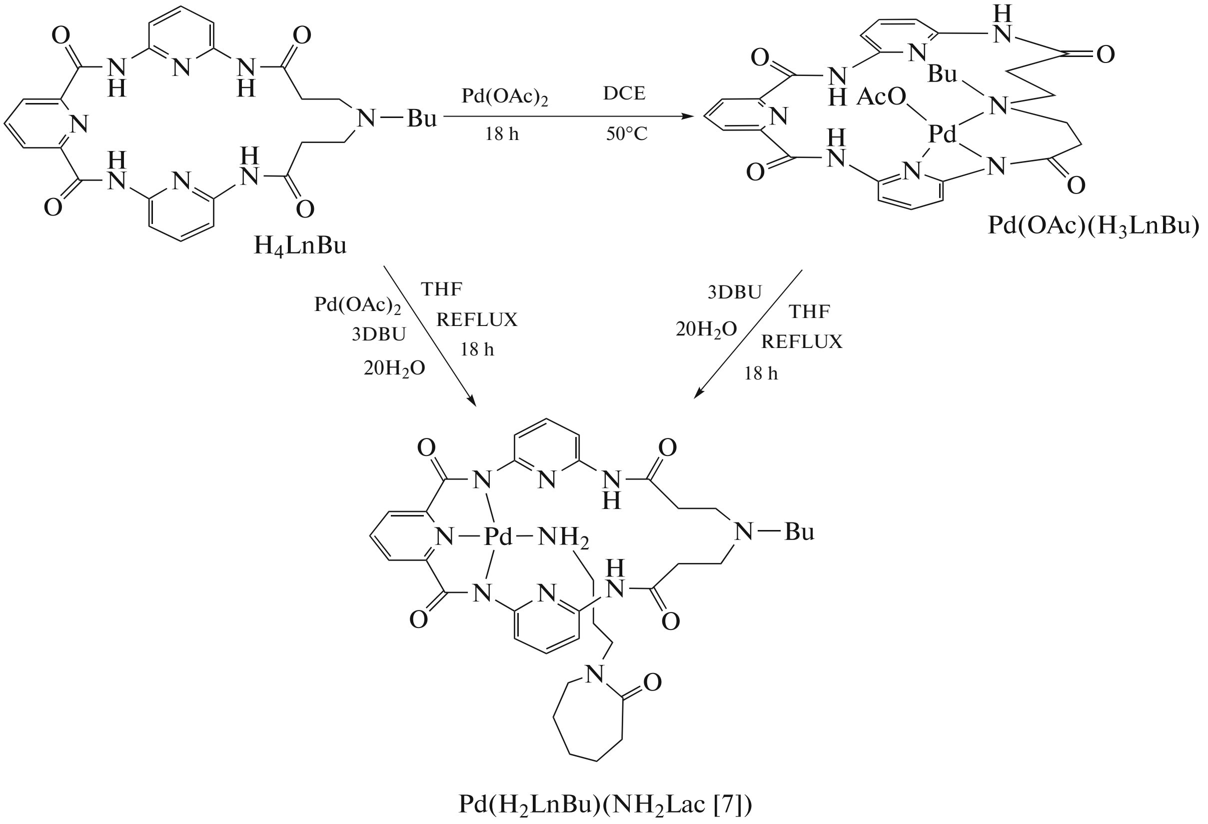
47

Kantam reported the synthesis of the palladium(II) complexes, in which metal is surrounded by mixed terdentate ligand containing negatively charged amido, carbocyclic carbene, oxime based O-donor and alkoxyl based ligand (**48**). The nucleophilic carbocyclic carbene ligands and anionic amidate, being strongly σ-electron donors, stabilize the oxidation of the palladiumin the heck and suzuki coupling reaction of benzene halides. The yield of the reaction is ~95% for the reaction involving aryl iodides and aryl boronic acid in 10 h at room temperature [46].



48

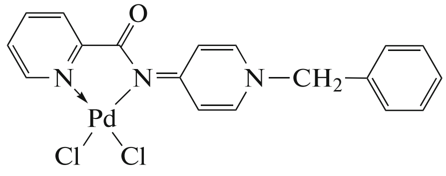
In 2014, we synthesized the new amide- and pyridine-containing macrocyclic ligand (H_4L_{nBu}) that contains two potential coordination pockets has been used to synthesize palladium complexes. Palladium coordinates to the head or tail region of H_4L_{nBu} to give the complexes $Pd(H_2L_{nBu})(NH_2Lac$ [7]) or $Pd(OAc)(H_3L_{nBu})$ depending on the conditions employed. $Pd(H_2L_{nBu})(NH_2Lac$ [7]) (which has palladium coordinated in the head region) can be made indirectly from $Pd(OAc)(H_3L_{nBu})$ by treatment with DBU and water in THF for 8 h. This indicated that it's the metal in the tail region that is the active form that eventually hydrolysed the water (Scheme 14) [47].



(Synthesis of amide- and pyridine-containing macrocyclic ligand and its palladium complexes)

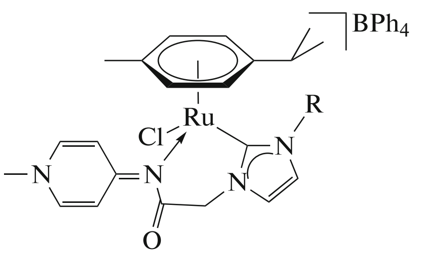
Scheme 14.

Pyridinium amidate. In 2011, we have successfully used pyridiniumamidate based ligand (**49**) in C–C suzuki and Heck coupling reactions [43]. Pyridiniumamidate 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. 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.



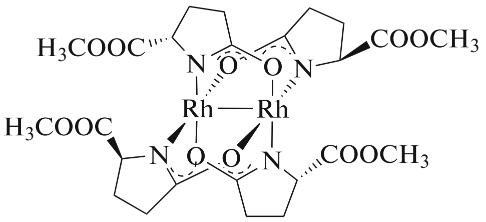
49

Wright and Albrecht synthesized ruthenium(II) complexes of pyridiniumamidate and N-heterocyclic carbene mixed ligands (**50**). These PYA-NHC complexes showed unique electronic properties in different solvents and as a result these complexes exhibited a range of catalytic activities in different solvents. In the catalytic dehydrogenation reaction of benzyl alcohol to benzaldehyde, the maximum conversion was 32% in DMSO solvent due to larger dielectric constant of this solvent ($\varepsilon_r = 46.7$) as compared to other solvents used [48].



50

Pyrrolidone and pyridonate. Doyle synthesized highly enantioselective, Rh(II) cyclopropanation catalysts (**51**) [49, 50]. The most efficient of them appeared to be methyl 2-pyrrolidone-5-carboxylate (Rh_2{(5S)-MEPY}$_4$) that gave up to 86% ee in the cyclopropanation of styrene with menthyldiazoacetate and up to 94% ee in the intramolecular reaction of allylicdiazoacetates. Furthermore, it was a very effective catalyst for the cyclopropenation of alkynes. Kenichi Fujita reported homogeneous perhydrogenation and dehydrogenation of fused N-heterocycles by iridium complexes (**52**) having pyridonate ligands. He used two complexes of iridium as catalyst. One complex contains bipyridonate ligand while other was monodentate ligand. Yield was totally depend upon number of donor groups attached to the iridium [51].



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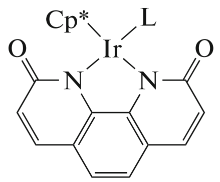


L = Pyridine
L = H_2O

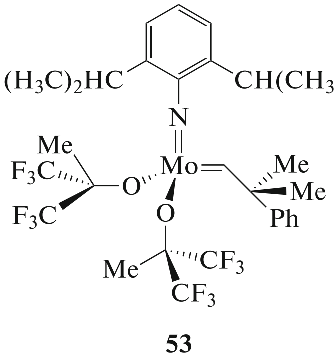
52

Imido and Nitrosyl

Both imido and nitrosyl are the group of nitrogen donor ligands usually with no pendant arms bound to the metal center.

Imido. Schrocksynthesized pseudo-tetrahedral imido complexes (**53, 54**) of molybdenum and tungsten in the formal oxidation state +6 [52]. The combination of sterically demanding amido, alkylidene and two bulky alkoxide ligands ensured sufficient stability of the complex against intermolecular ligand scrambling or other decomposition reactions. Because of the relative electron-deficiency of the metal center, a strong donation of the nitrogen lone pair to the metal took place and this caused an apparentsp hybridization at the nitrogen atom, which in turn resulted in an MNC angle approaching 180°. Schrock applied this catalyst successfully for ROMP.

N. Kotohiro et al. worked on (imido) vanadium(V) dichloride complexes [$V(NR')Cl_2(L)$] containing imidozolin-2-iminato and imidazolin-2-iminato ligands (**55**) and they were used as catalyst precursors for ethylene copolymerization. All complexes showed high catalytic activity for ethylene polymerization in diethylaluminium chloride (Et_2AlCl) as compare to methylaluminoxane (MAO) due to short V–N–C bond angles and having tetrahedral geometry around the vanadium atom. Upon increasing steric bulk, polymerization temperature and concentration of norbornene (NBE), the catalytic activity was decreased. Therefore, reactions were done at 60°C. If more electron donating substituents were attached, activity of polymerization increased. NBE contents can be controlled by ethylene concentration. While if 5-ethylidene-2-norbornene (ENB) was used instead of NBE, catalytic activity increase. The yield obtained under optimum conditions was 50 mol % [53].



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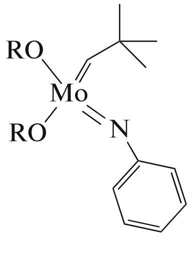

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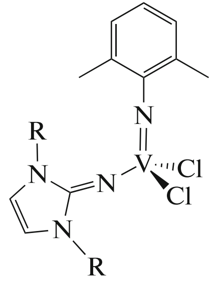
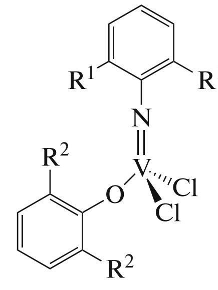


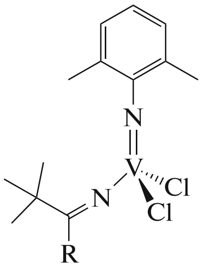
R = *t*-Bu

55

Zhang synthesized (arylimido)vanadium(V) complexes (**56–61**) containing anionic ancillary donor ligands of type, $V(NAr)Cl_2(L)$ (Ar = 2,6-$Me_2C_6H_3$, L = aryloxo, ketimidephenoxyimine) [54]. These complexes exhibited high catalytic activities for ethylene polymerization in the presence of Al cocatalyst; $V(NAr)Cl_2(O$-2,6-$Me_2C_6H_3)$ showed the exceptionally high activities in the presence of halogenated Al alkyls, such as Et_2AlCl, $EtAlCl_2$, etc. (Arylimido)vanadium(V)-alkylidene complexes, $V(CHSiMe_3)(NAr)(L)$ (L = $N{=}CtBu_2$, O-2,6-*iso*-$Pr_2C_6H_3$) exhibited the remarkable catalytic activities for ring-opening metathesis polymerization of norbornene. (Imido)vanadium(V) complexes containing the (2-anilidomethyl)pyridine ligand, $V(NR)Cl_2[2\text{-}ArNCH_2(C_5H_4N)]$ (R = 1-adamantyl, cyclohexyl, phenyl, Ar = 2,6-$Me_2C_6H_3$, 2,6-*iso*-$Pr_2C_6H_3$), exhibit the remarkable activities for ethylene dimerization in the presence of MAO, affording 1-butene exclusively (selectivity 90.4 to 99%). The steric bulk of the imido ligand plays an important role in the selectivity, and the electronic nature directly affects the activity.


R^1 = Me, *iso*-Pr
R^2 = Me, *iso*-Pr, *t*-Bu

56


R = *t*-Bu (a), CH_2SiMe_3 (b)

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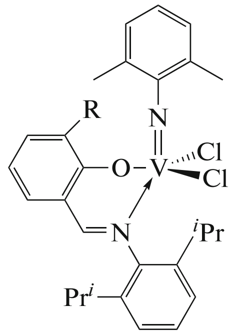
R = H, Me, *t*-Bu

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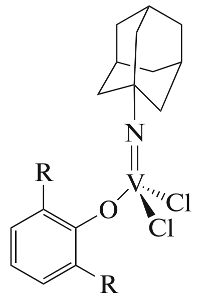
R = Me, *iso*-Pr

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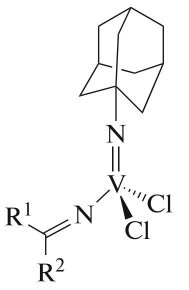
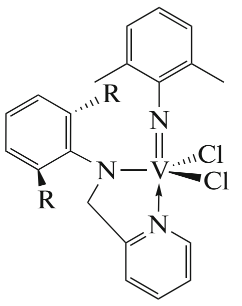

R^1, R^2 = *t*-Bu; *t*-Bu, *t*-Bu; CH_2SiMe_3, *t*-Bu; Ph

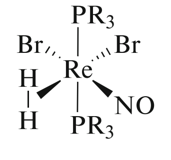
60


R = Me (a), *iso*-Pr (b), F (c)

61

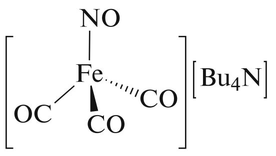
Nitrosyl. Yanfeng Jiang and Heindz Berke reported the donating capability of nitrogen in different nitrosyl ligands and their applications in homogeneous catalysis. They reported the ancillary properties of nitrosyl ligands that showed the *trans* effect, the linear and bent transformations. In linear donate two electrons like CO and formed the complex with metals and in bent fashion donate electron pair just like –N=NR showed sigma donating and single face π donating capabilities, as in rhenium mononitrosyl (**62**) and dinitrosyl and in iron mononitrosyl (**63**) and dinitrosyl (**64**) catalysts reported in this mannar. These redox active ligands catalysed the hydrogenation as Noyori ruthenium based asymmetric hydrogenation and grubbs-shraken reactions. These homogeneous catalysis showed the high degree of selectivities including chemoselectivities, regioselectivities, diastereomeric and enentiomeric selectivities [55].

Balz Dudle et al. synthesized rhenium nitrosyl complexes (**65**) $[ReBrH(\eta^2\text{-}C_2H_4)(NO)(P\frown P)]$, [ReBr(Et)(MeCN)(NO)(P⌒P)], and [$ReBr(C_2H_4)(NO)(C_6H_4$-sixantphos)] by reaction of [$ReBr_2(MeCN)(NO)$(P⌒P)] with $HSiEt_3$ in the presence of ethylene. P⌒P is large chelate diphosphine substitutent and ethylene considered as most suitable ligand as it had very small size and appropriate capabilities to Re centers which is rich in electrons. These complexes were used as precatalysts in the olefin hydrogenation. 1-Hexene and styrene were used for the studies of their catalytic activities which showed that activities of rhenium catalysts could be very dependent on the choice of medium used in the reaction. Moreover comorthometalaplexes of ted sterioisomers were found to be moderately active in the hydrogenation of disubstituted substrates that were more sterically demanding but ethylene hydride complexes were inactive. On the basis of these results a mechanism was suggested that was an Osborn type hydrogenation because it had more affinity of suitably substituted rhenium centers to the hydrogen and olefins. These properties were facilitated by tuned ligand sets and also supported by large-bite-angle diphosphines [56].



R = *iso*-Pr, Cy

62



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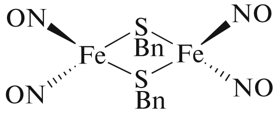

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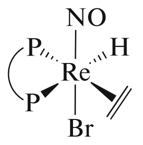


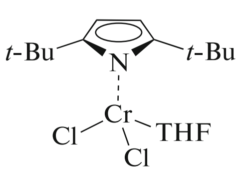
65

Azole

In this class, we discuss those metal complexes in which donor ligand constitutes at least five membered ring with one donor atom (one nitrogen called pyrrole) and with two donor atoms may be similar (two nitrogens together called pyrazolyl or separated by a carbon called imidazole, benzimidazole) or different (one nitrogen with other atom like oxygen called oxazole or sulphur called thiazole) and finally with three donor atoms (three nitrogens together called triazole).

Pyrrole and porphyrin. S. Licciulli et al. synthesized chromium species, i.e., [$\{\eta^5$-$(^tBu)_2C_4H_2N\}CrCl_2(THF)$] (**66**). It was prepared by deprotonation of 2,5-di-*tert*-butylpyrrole with [$CrCl_3(THF)_3$]. This specie was precatalyst for selective trimerization of ethylene and produced hexane in excellent yield with small amount of isomerization. Small amount of $AlCl_3$ was used as activator. The factors which affected the above catalytic reactions were temperature, activator and catalysts loadings [57]. Titanium pyrrole catalysts (**67**, **68**) have been synthesized for hydroamination reactions [58, 59].

Metal complexes of pyrrole with pendant imine or oxazoline are important homogenous catalysts. Sun and its co-workers synthesized Ni(II) and Pd(II) complexes (**69**) based on N-(1*H*-pyrrol-2-yl)methylene)-2-(diphenylphosphino)benzenamine [60]. The metal coordinated to nitrogen and phosphorus in a distorted square planar geometry. Upon treatment with modified methylaluminoxane (MMAO), the [NNP]NiX complexes were robust and exhibited high activity for the vinyl addition polymerization of norbornene. Gade and its coworkers used bis(oxazolinyl)pyrrole as a new monoanionic tridentate supporting ligand in the synthesis of a highly active palladium catalyst (**70**) for Suzuki coupling reactions [61]. This dinuclear complex was formed by the reaction of pyrrole-2,5-bis(carbonitrile) with 2-amino-2-methyl-1-propanol, the protonated ligand formed was deprotonated and treated with palladium cyclooctadiene dichloride.



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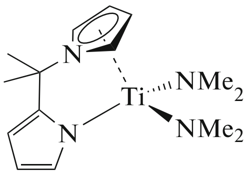

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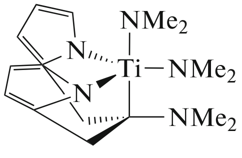

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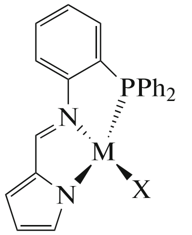

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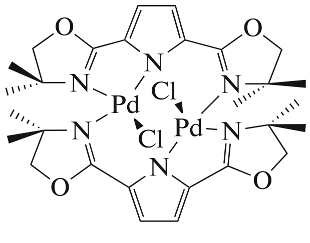
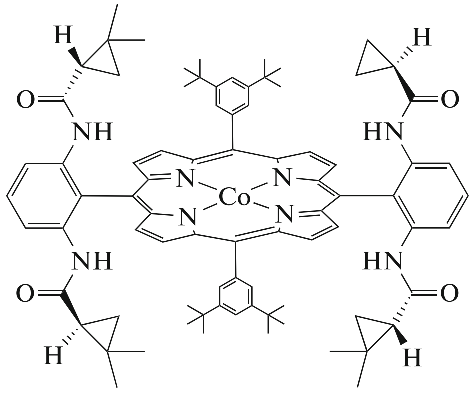


70

Doyle prepared a chiral cobalt(II)-porphyrin catalyst (**71**) which showed exceptional selectivity in cyclopropanation reactions [62], with olefins this catalyst can convert nitrodiazoacetates into the corresponding cyclopropanes, which provide convenient access to cyclopropyl amino acids and cyclopropyl amines. These transformations are performed stoichiometrically without high dilution and at room temperature and this catalyst has full diastereo control for the *trans* isomer. Crabtree was successful in executing selective epoxidation of alkenes with a newly synthesized magnesium porphyrin catalyst (**72**), that uses hydrogen bonding between the carboxylic acid on the substrate molecule and a Kemp's triacid unit [63]. In 2009, Guo synthesized the iron porphyrin (**73**) that can catalyse cyclohexane oxidation with PhIO. It was found that the catalyst worked best when R^1 = H and R^2 = Cl [64].



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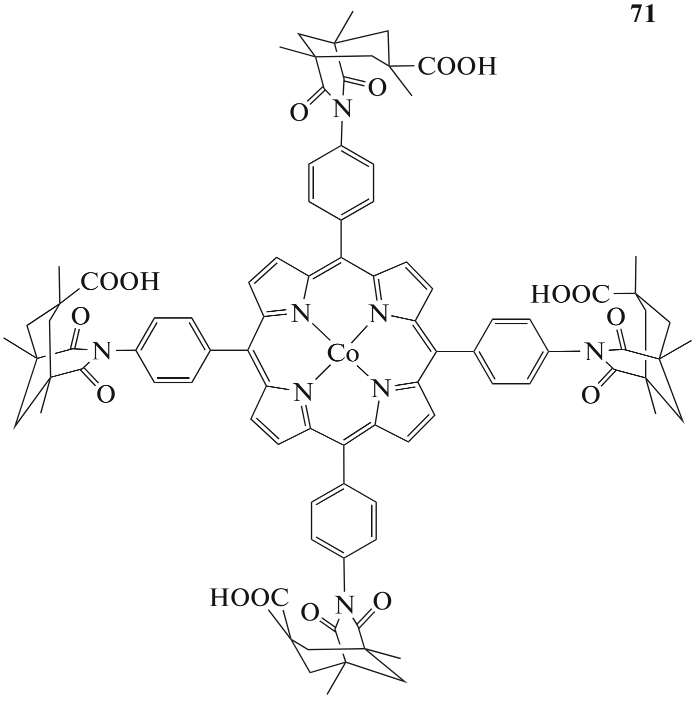

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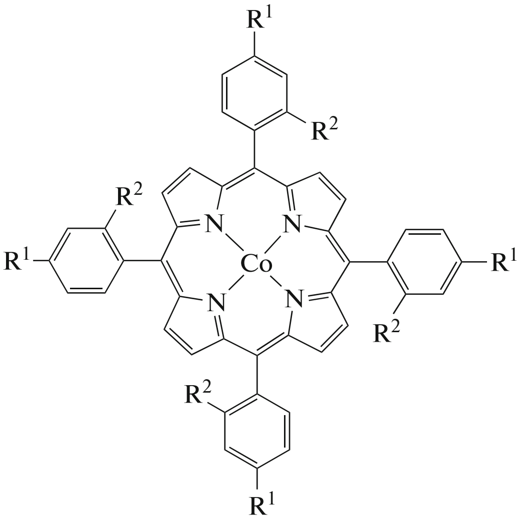
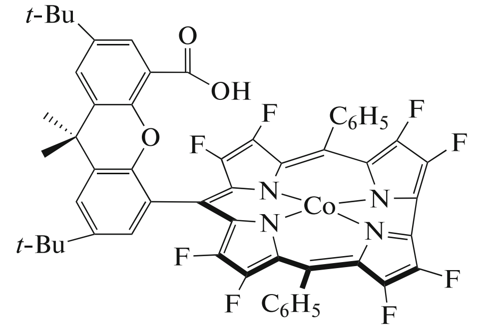


73

G. Daniel et al. found out that complexes with 5,15-*bis*-pentafluorophenyl substitutient are very effective oxygen evolving reaction (OER) catalyst. He synthesized cobalt hangman β-octafluorocorroles as OER catalyst (**74**). This catalyst was very stable under given operating conditions and evolved only O_2 as the OER product at the modest overpotential. The ability of hanging group to pre-organize water within this hangman cleft appeared to be very helpful for the formation of O–O bond. Oxygen atoms present in molecules might be situated within the hangman cleft; one H_2O molecule situated in the primary coordination sphere and another H_2O molecule in secondary coordination sphere through hydrogen bonding to hanging group. In order to increase the oxidizing power of corrole subunit they modified macro-cycles by using electron withdrawing groups in corrole. This β-octafluorohangman corrole was synthesized in overall 23% yield. Importantly it was noted no CO_2 produced during electrolysis which might happen if this corrole framework oxidized [65]. In the same year, Z. Halime et al. explained the homogeneous catalytic reduction of O_2 to H_2O. Synthetic analogue of the heme a_3/Cu_B (heme/copper) site in cytochrome-C oxidase (ligand-FeCu) (**75**) or its copper free complex (ligand-Fe) (**76**) in acetone was used as catalyst. This homogeneous catalytic system was studied in detail, an intermediate was detected spectroscopically at room temperature and found that the rate of the O–O bond cleavage of Fe(III)–OOH specie was observed with either LFeCu or LFe catalysts was nearly same (at –60°C, this is rate determining step), whereas rate of O_2 binding to LFeCu was comparatively faster than that for LFe (at –60°C, this is no more rate determining step). Reaction of reduced form of $[LFe^{II}Cu^{I}]^{+}B(C_6F_5)^{-}$ with O_2 resulted in the formation of low-temperature stable LFe(III)-μ-peroxo-Cu(II) complex. Thermal decomposition of $[LFe^{III}–(O_2^{2-})–Cu^{II}]^{+}$ complex released half equivalent of O_2 to generate an Fe(III)-μ-oxo-Cu(II) complex ($[LFe^{III}–O–Cu^{II}] + B(C_6F_5)_4^{-}$). Decamethylferrocene (Fc*) used as one electron donor and trifluroacetic acid as a proton source [66].



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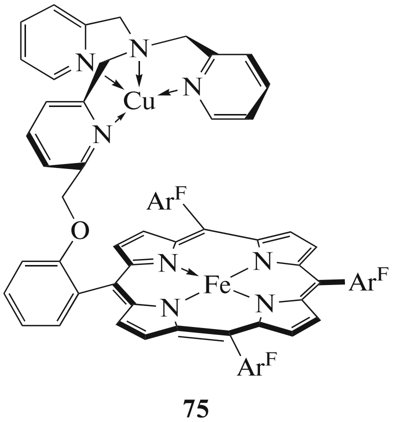

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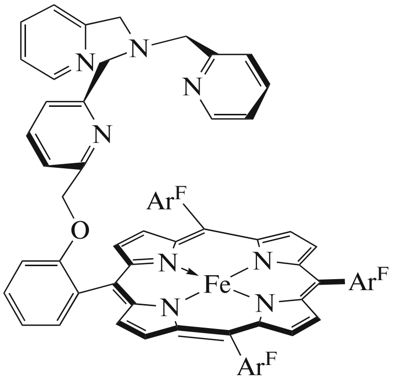
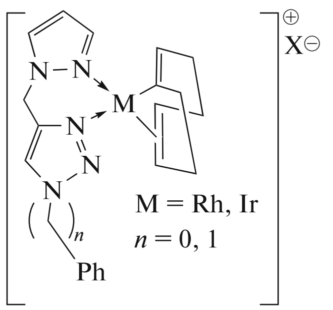


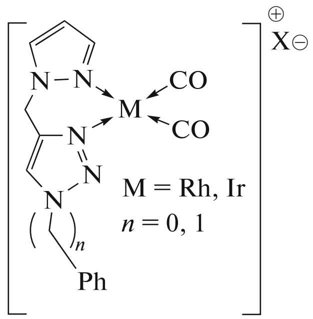
76

Pyrazolyl and triazole. A. Messerle reported the homogenous catalysts of rhodium(I) and iridium(I) in which the ligands used were pyrazolyl-triazolyls (**77**, **78**). These complexes formed distorted boat conformation with M–N (pyrazole) bonds longer then M–N (triazole) reflecting stronger donor ability of triazolyl species. 4-Pentyn-1-amine has converted to 2-methyl-1-pyroline (mostly with TOF_S > 400 h^{-1} at 60°C) by hydroamination reactions which have successfully catalyzed by all these complexes. During the reaction of 4-pentyn-1-amine the iridium complexes with tetrakis[(3,5-trifluoromethyl)phenyl]borate ($BAr_4^{F^-}$), were more active (TOF^d = 453 h^{-1}) than rhodium complexes with BPh_4^-counteranion (TOF^d = 22 h^{-1}). Dicarbonyl complexes have effectively catalyzed intramolecular cyclization of non-terminal alkynamines to cyclic imines and alkenamines to cyclic amines (TOF^e = 9.5 h^{-1} for PyT and 43 h^{-1} for PyS) through hydroamination reaction [67]. Pyrazolyl borates are among the important nitrogen donor groups, especially in homogeneous catalysis. For example, **79**–**82** acted as catalysts for the olefin aziridination reaction and **83** was a good catalyst in the ethylene polymerization reaction [68].



N–N = PyT or PyS, and X = BPh_4^- or BAr_4^{F-}

77



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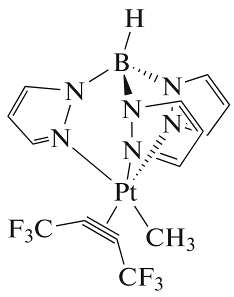

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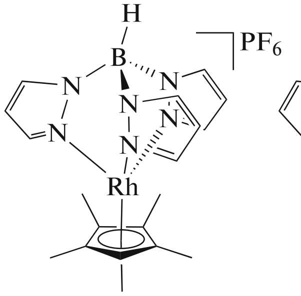

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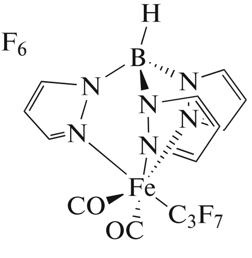

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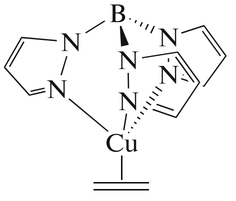

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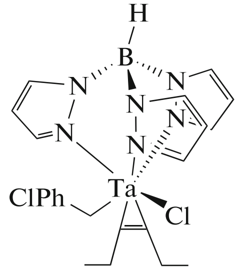
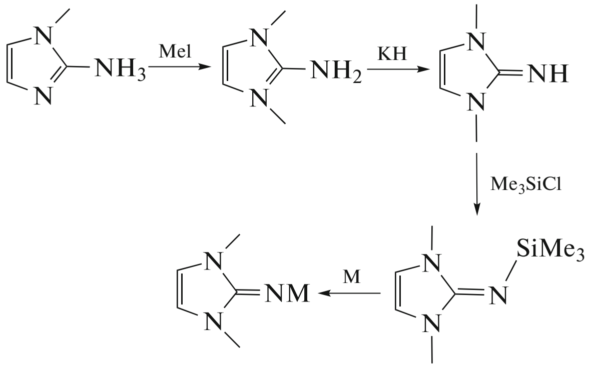
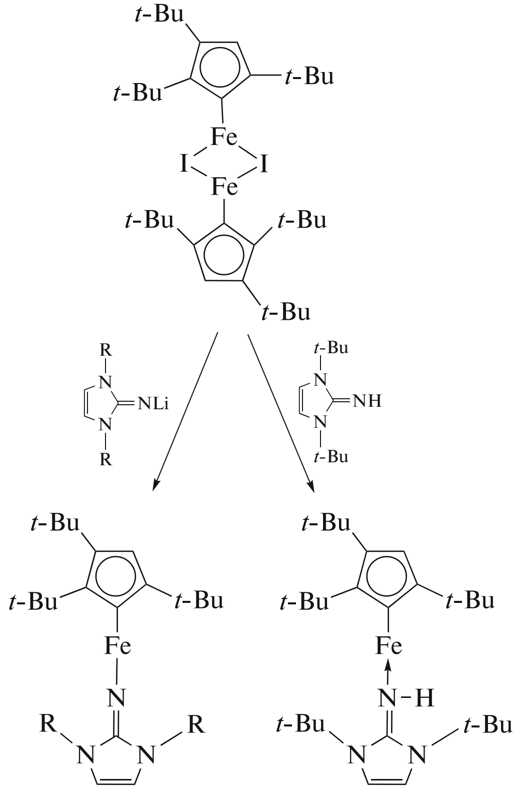


83

Imidazole and benzimidazole. Xian Wu and its co-workers reported the work related to imidazolin-2-iminato and imidazolin-2-imine. They synthesized these ligands by the reaction of organic azides and nitrogen-hetrocycliccarbene. They also explored the coordination complexes (Scheme 15) of this ligand with several metals like Ti, Zr, V, Cr, Mo, Rh, Re, Ni, Pd, Fe (Scheme 16), Cu and with *f*-block elements. These complexes were used in homogeneous catalysis like alkyl metathesis and olefin polymerization [69].



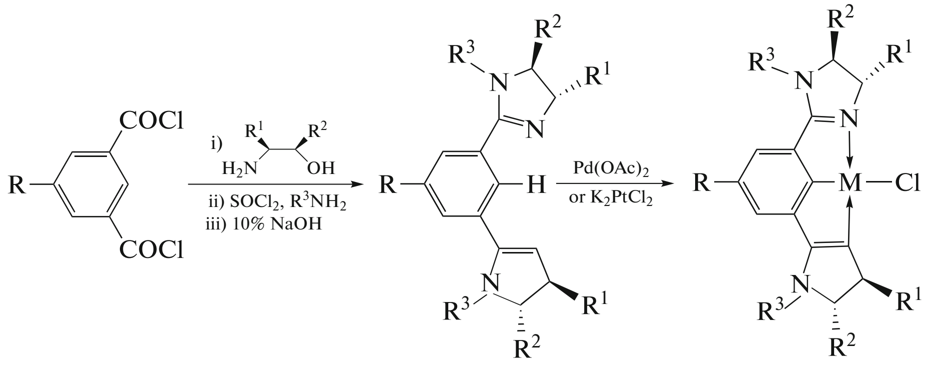
Scheme 15.



(Synthesis of iron(II) complexes; R = *t*-Bu or Dipp)

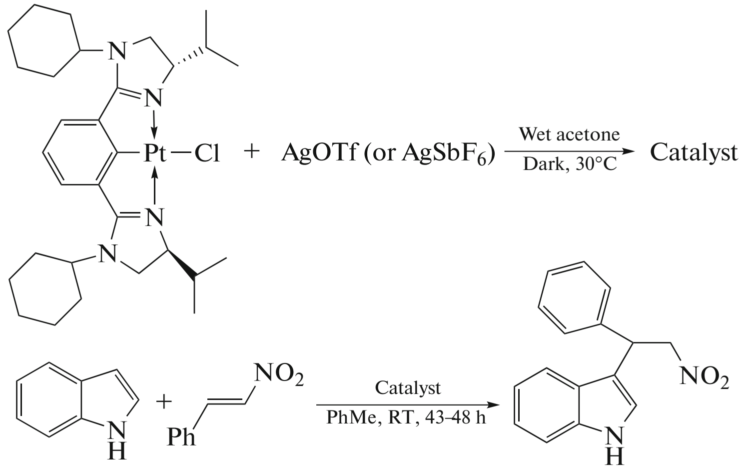
Scheme 16.

Imidazole stabilised with phenyl group is common in homogenous catalysis. Song and Gong et al. synthesized symmetrical bis(imidazoline) NCN pincer metal complexes. Tridentate bis(imidazoleinyl)phenyl ligand complexes of palladium and platinum were synthesis via direct C–H bond activation, as shown in Scheme 17. Palladium-NCN pincer acts as a catalyst for suzuki coupling reaction, on the other hand, platinum-NCN pincer acts as catalyst for asymmetric allylation of 4-nitrobenzaldehyde or 4-nitrobenzene sulfonimine with allyltributyltin. Cationic platinum-NCN pincer type catalyst (obtained by abstraction of chloride from Pt–NCS neutral complex upon treatment with AgOTf or $AgSbF_6$) can catalyse the unsymmtric friedel-crafts alkylation in which indole reacts with *trans* β-nitrostyrene (Scheme 18) [70]. In 2012, Jianliang Xiao and its co-workers reported that bifunctional Cp*IrCl(N^C) containing cyclometallated iridium(III) complex (one of the example is **84**) based on 2-aryl imidazoline ligands were found to be excellent catalysts for the decomposition of HCO_2H–NEt_3 mixtures to give H_2 and CO_2 under normal conditions. In the presence of catalyst no CO formations occur. The modular structures of the catalysts had the ability to construct the structure activity relationships for the complexes, leading to the rational optimization of the catalyst structure. The iridium complexes were formed in good yields by possessing excellent stability, not necessary to protect from the air. A donor group nature had a dramatic role on the catalytic reaction. During the dehydrogenation of formic acid reaction the lifetime of the active catalysts totally depend on the N-donor group. Evidence showed that remote NH functionality was crucial in catalysis, without this there was no dehydrogenation. Formic acid has dual role; firstly, it acts as a hydride and secondly, it is proton source. The NH proton was not able to directly protonate the Ir–H hydride, nor HCO_2H. Instead of this a HCO_2H assisted-proton hopping might occur, nitrogen donor atom played role in the protonation of hydride that resulted in H_2 release by dehydrogenation of formic acid [71].

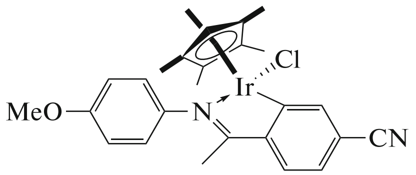


(Preparation of the bis(imidazolinyl)phenyl, anionic tridentate
(R = H, R^1 = *iso*-Pr, R^2 = H, R^3 = *p*-$CH_3C_6H_4$))

Scheme 17.

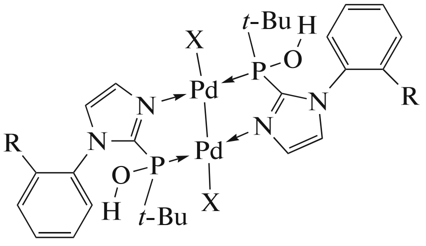


Scheme 18.

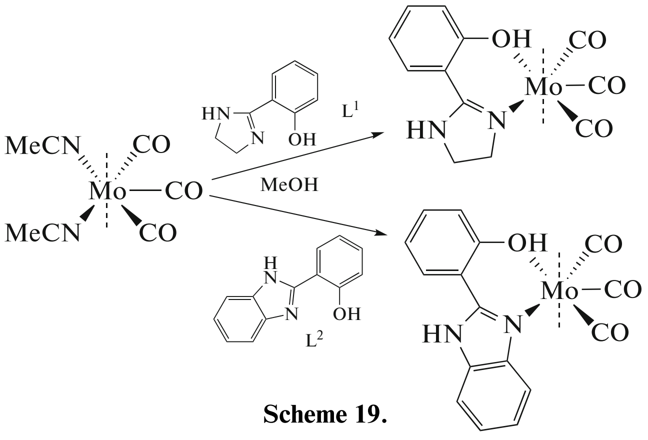


84

D.F. Hu et al. synthesized imidazole palladium complexes with pendant phosphone donor moiety precisely known as 2-(*tert*-butylhydrophosphoryl)-1-(2-R-phenyl)-1*H*-imidazole (**85a**, R = H; **85b**, R = OMe) [72]. The tautomeric form of this oxide on reaction with Pd(COD)Cl_2 (or $PdBr_2$) produced monopalladium-bis(2-(*tert*-butylhydrophosphoryl)-1-(2-R-phenyl)-1*H*-imidazole)PdX_2 (R = H, X = Cl; R = OMe, X = Br) and dipalladium [μ_2-2-(*tert*-butylhydrophosphoryl)-1-(2-R-phenyl)-1*H*-imidazole-N,P)PdX$]_2$ (**85a**, R = H, X = Cl; **85b**, R = OMe, X = Br). The crystal structure of **85a** showed that five atoms (PdPd-NCP) were not in plane but they formed the geometry that was pentagone cyclopentane. However, both palladium showed nearly square planner geometry. These palladium complexes were used as catalyst in suzuki-miyaura cross coupling reactions. In this reaction, it was Pd(0) which performed catalytic activity through the disproportionation of dipalladium compounds in solution and ligands showed excellent efficiencies because of being air and moisture stable [72]. M. Calhorda synthesized $[MoI_2(CO)_3(L_1)]$ and $[MoI_2(CO)_3(L_2)]$ having ligands named 2-(2'-hydroxyphenyl)imidazoline (L^1) and 2-(2'-hydroxyphenyl)benzimidazole (L^2). The synthesis of these complexes is shown in Scheme 19. These complexes were immobilised on stiffened bandages with the help of MCM-41 and silica by grafting (3-chloropropyl)trimethylsilane. The NMR technique examined that the nitrogen donor ligands were in neutral configuration in both complexes. These complexes were selectively used for the 100% epoxidation of ciscyclooctene [73].

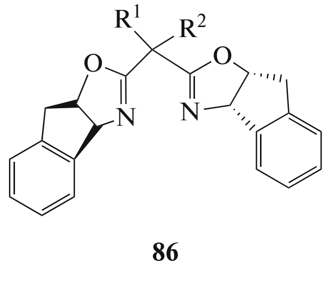


85a: R = H, X = Cl **85b**: R = OMe, X = Br

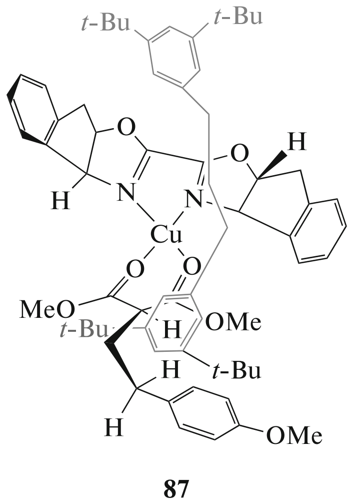


Scheme 19.

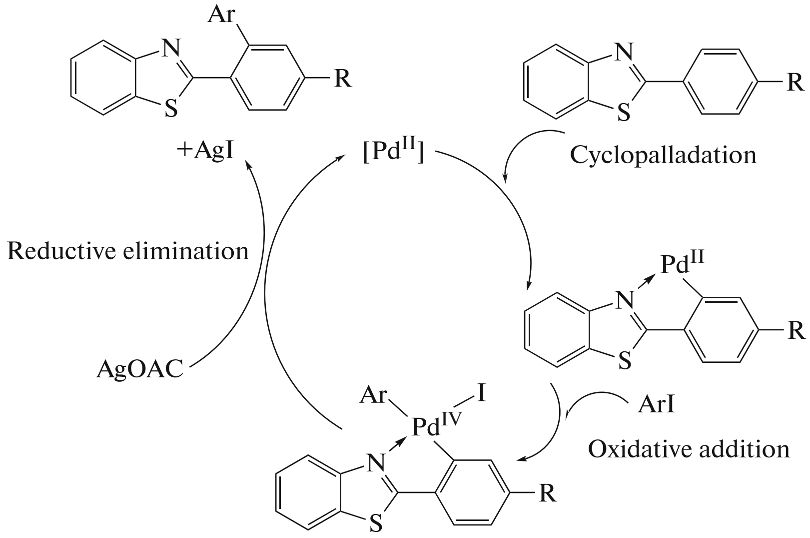
Oxazole and thiazole. H. Xiong et al. studied tridentate bis(oxazoline) based (BOX), ph-DBFOX and Ph-PyBOX ligands (**86**) and use of their copper complexes in cyclopentannulation of indoles. These catalysts become selective upon introduction of nitrones, aldehydes or imines into cyclopropane (**87**). They also found out that if electron donating groups were attached, catalytic activity increased significantly as it increased lewis acidity but decreased stereo-selectivity. When electron donating bulky groups were attached, selectivity decreased due to steric and electronic hindrance. However, electron withdrawing groups increased the selectivity on the cost of catalyst efficiency [74]. In 2012, Q. Ding and its coworkers studied Pd(II) catalyzed direct *o*-arylation reactions of benzothiazoles with aryl iodide via benzothiazole directed C–H activation that is an unusual to the traditional strategy. Initially the coupling of 2-phenylbenzothiazole with 1-iodo-4-methylbenzene in the presence of $Pd(OAc)_2$ gave the product in small amount. However, at the larger amount of $Pd(OAc)_2$ in the presence of catalyst, the yield of the product is 41% but there is no reaction without the catalyst. A possible mechanism for the reaction of 2-arylbenzothiazole is shown in Scheme 20. The proposed catalytic cycle involves the following steps: cyclo-palladation of 2-arylbenzothiazole via C–H bond activation; oxidation addition of palladium(II) to palladium(IV); reductive elimination affording mono-arylated product and palladium(II); the monoarylated product could re-enter the cycle to ultimately yield the corresponding di-arylated compound [75].



86



87



(Possible mechanism for Pd-catalyzed directed arylation with Ag(I)/Ar–I)

Scheme 20.

SUMMARY

A strategy that uses supramolecular interactions to direct catalysis and which is amenable to combinatorial chemistry is surprisingly under-developed at this point in time. This concept is borrowed from the natural world, in which non-covalent interactions direct subtle but powerful forces towards the construction of architectures, such as the DNA helix. Pertinently, reversible interactions are the bread and butter of biological catalysis, finding particular use in cellular enzymatic processes. Knowledge of homogeneous catalysis at the metal centers of model complexes is based upon the progress and understanding of their chemistry and reactivity. The stability and the selectivity of a catalyst are strongly related to its molecular structure. Ligands play an important role in tuning the properties of metal complex in homogeneous catalysis. The ligand design and properties, such as electron donor tendency, back bonding, *trans* effect and steric bulk play a vital role in directing the reactivities of the many complexes. Many variables influence the catalytic activities such as reagent gas pressure, solvent, temperature, amount of catalyst, and type of co-catalyst.

Variety of nitrogen donor ligands combine with various metals provided new dimensions in catalytic homogeneous reactions from 2011 to early 2014. Palladium complexes of most nitrogen donor ligands were used for suzuki, heck, stille and hiyamma cross coupling reaction. Amines complexes of Zn, Ru and Ni were used as catalysts for oxidation of epoxides and carbonyl containing organic compounds. Imines complexes with Co, Ni and Pd were used for oligomerization and polymerization of olefins, Cr and Mn imines complexes for carbondioxide addition in styrene and asymmetric epoxidation respectively. Ru-hydrazone for carbonyl hydrogenation, Ni/Co-oxime for hydrogen evolution at low voltages from non aqueous solutions. Rh-iminophospharanes for hydrogenation of carbonnyl, Mo-imido for ROMP, V-imido for ethylene polymerization, Re/Fe-nitrosyl for olefin hydrogenation. Amido and amidate based ligands were also used during this period in homogenous catalytic reactions. Cr/Ti/Hf/Zr-amido for olefin polymerization, Ag-amido for cycloaddition, Fe/Co/Ir-amido, Ni-amidohydoaminiation, dehydrogenation, C-C cross coupling. Ni-PYA for C-F activation, Pd/Zn-amidate for reduction of carbonyl and azo compounds, Ru-PYA for dehydrogenation of alcohols, Rh-pyrrolidone and Ir-pyridonate for cyclopropanation and dehydrogenation reactions respectively. Azoles complexes with various metals are used for polymerization, suzuki coupling and for hydrogen aminiation reactions. Substituted porphyrrins complexes are used as catalyst for OER and for oxidation of organic compounds.

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