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REVIEW

NHC–metal complexes based on benzimidazolium moiety for chemical transformation

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Abstract N-heterocyclic carbenes (NHC) are now commonly encountered in organometallic and inorganic coordination chemistry because of its environmental friendly nature as solvent and catalyst, high activity, selectivity and easily recovered materials that were used to replace the traditional volatile organic solvents which generally suffered from environmental problems. Benzimidazole based ionic liquids (BILs) offering a new possibility for developing environmentally-friendly basic catalyst with transition metal and non-transition metal (Ag, Au, Ru, Rh, Fe, Co, Cu, Cd and Pd). They are flexible, nonvolatile, noncorrosive and immiscible with many organic solvents. In this review, we wish to present an overview of the preparation and applications in various reactions like alkylation, arylation, etherification, benzoin reaction, aldol condensation and metal mediated catalyst in Suzuki, Suzuki–Miyaura, Heck cross coupling and reduction, also in electrochemical application (electrocatalyst), anion sensor, solar cell, proton conduction, malaria parasite, antimicrobial activity, etc.

Contents

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1. Introduction

Compounds composed of ions that exhibit low melting points (usually below 100 °C) have come to be known collectively as ionic liquids (ILs). These salts have extremely low vapor pressures, wide liquid range, good electrolytic properties with large electrochemical window, tunable polarity and are easy to recycle. They therefore have received great attention as potential solvents to replace volatile organic solvents in a wide variety of chemical reactions, separation and manufacturing processes to provide excellent protocols for clean and green ideology (Welton, 1999; Wilkes, 2002). Since ionic liquids (ILs) have quite unique properties and can be used as solvents in organic synthesis, electrolytes in electrochemistry and catalysts in catalysis chemistry, they recently gained a lot of attention from both chemists and physicists (Wasserscheid and Keim, 2000).

Many transition-metal complexes dissolve readily in ionic liquids, which enable their use as solvents for transition-metal catalysis. Sufficient solubility for a wide range of catalyst complexes is an obvious but not trivial, prerequisite for a versatile solvent for homogenous catalysis. Some of the other approaches to the replacement of traditional volatile organic solvents by "greener" alternatives in transition-metal catalysis and these new materials show additional intrinsic magnetic, spectroscopic or catalytic properties depending on the enclosed metal ion (Jin et al. 2005; Chiou et al., 2006).

During the past decades N-heterocyclic carbenes (NHCs) have emerged as a versatile class of dative ligands in metal coordination chemistry because NHCs provide an electron-rich metal center with a thermally robust metal–ligand bond. The use of polydentate NHC ligands has allowed the preparation of novel complexes whose stability is entropically increased by the chelate effect, particularly in the field of homogeneous catalysis. The metal–NHC complexes exhibit excellent catalytic activity for many practically useful organic transformations, notably the C–C (Kantchev et al., 2007) and C–N cross coupling reactions (Broggi et al., 2008; Winkelmann et al., 2009), C–H bond activation as well as the extremely useful metathesis reaction (Ritter et al., 2006).

The first NHC, derived from benzimidazole, N,N′-bis (2,2-dimethylpropyl) benzimidazolylidene, was isolated in 1998 by reduction of thione. Since the discovery of free N-heterocyclic carbene (NHC) (Arduengo et al., 1991), organometallic chemistry based on benzimidazolium ILs has been receiving considerable attention. The primary characteristic of NHCs is that they are strong σ-donor ligands, which can bind firmly to different metal ions with various oxidation states (Danopoulos et al., 2007) and a variety of related transition–metal complexes have been synthesized through deprotonation of N,N′-disubstituted benzimidazolium salts (Hahn et al., 2007). They are good carbene-transfer agents for the synthesis of Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru carbene complexes, such a route affords a convenient method for the preparation of these metal carbene complexes (Lee et al., 2005). Also metal–NHC complexes have been demonstrated to be efficient catalysts for some organic reactions, such as Heck, Suzuki, Kumada cou-

plings and olefin metathesis (Gade and Laponnaz, 2007; Sommer and Weck, 2007; Schneider et al., 2007). N-heterocyclic carbene complexes have shown to be remarkably stable toward heat, air and moisture.

In this article, we reviewed metal-containing ionic liquids and ionic liquid crystals based on benzimidazolium moiety (including closely related other azoliums), that is metal complexes of benzimidazolium salts with IL properties. They have been realized as versatile reaction media, catalyst, catalyst precursors and reagents for various chemical processes.

2. NHC–Ag complexes

There is at present a broad range of structural motifs for the benzimidazolium based NHC–Ag complexes being applied in catalytic processes. Each of these complexes has its own characteristics that can be adjusted for optimal performance and the interplay of all of them specifically modulates electronic and steric properties, reactivity and catalytic patterns.

2.1. Anion exchange

N,N′-dibutylbenzimidazolylidene silver complexes of chloride, cyanide and nitrate have been synthesized (Huang et al., 2007) by reaction of N,N′-dibutylbenzimidazolium iodide with Ag_2O through abstracting Cl^- and CN^- anions from solvents CH_2Cl_2 and CH_3CN, respectively, or in the presence of NO_3^- anion in reaction mixture (Scheme 1). Crystal structures of N,N⁻-dibutylbenzimidazolylidene silver chloride, bromide, cyanide and nitrate were determined, unmistakably confirming the iodide/anion exchanges. The possible rationale for the iodide/anion exchanges lies in the instability of benzimidazolylidene silver iodides. The iodide/anion exchange route possibly represents a practical route to prepare a diversity of benzimidazolylidene silver complexes with a non-iodide anion part from readily available benzimidazolium iodides and silver(I) oxide, especially when the benzimidazolium salts are difficult to access.

2.2. The oligoether linked as PTC

Polyether chain phosphine containing metallocrown has been widely studied, because in the complexes the presence of weakly binding oxygen-donor groups can significantly increase
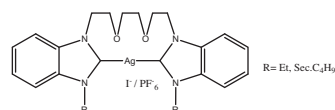
Figure 1   Silver(I) macrocyclic complexes.

the catalytic performance of these systems (Barnard et al., 2004). The NHC complexes containing metallocrown ethers have structural similarity with related phosphate complexes and they have potential application as a catalyst and a phase-transfer reagent.

Liu et al. (2007) reported 1,10-[1,2-ethanediylbis(oxy-1, 2-ethanediyl)]bis[(3sec-butyl)benz-imidazolium-1-yl]iodide, 1, 10-[1,2-ethanediylbis(oxy-1,2-ethanediyl)]bis[(3-ethyl)benzimi-dazolium-1-yl]iodide and 1,10-[1,2-ethanediylbis-(oxy-1,2-eth-anediyl)]bis[(3-secbutyl)benzimidazolium-1-yl]hexafluorophos-phate and their three new silver(I) macrocyclic complexes (Fig. 1) containing NHC metallacrown ethers, benzimidazole ring head-to-tail p–p stacking interactions are observed due to intermolecular I—H–C hydrogen bonds.

### 2.3. Bis-benzimidazolium dibromide for transmetallation

Ganapathi and Kandasamy (2007) reported that the reactions of N-isopropyl benzimidazoles with either benzyl bromide or 2,4,6-trimethyl benzyl bromide afforded the expected benzimidazolium salts. However, the reaction of N-isopropyl benzimidazole with tert-butyl bromide results in an unexpected benzimidazolium bromide. The products show a very low melting point without decomposition which suggests that they belong to the category of ionic liquids. Further, the treatment of N-isopropyl benzimidazole with 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene yielded 1,1-di(isopropyl)-3,3′-(mesityl-dimethylene)-dibenzimidazolium dibromide which on further treatment with Ag_2O gives (**2a**) Scheme 2.

2.4. Reference electrode in electrochemical application

Commonly used reference electrodes for various electrochemical measurements performed in acidic medium. However, when using the Ag/AgCl reference electrode in alkaline media-based electrochemical measurements, it could be extracted as silver oxide complexes which could result in a large error
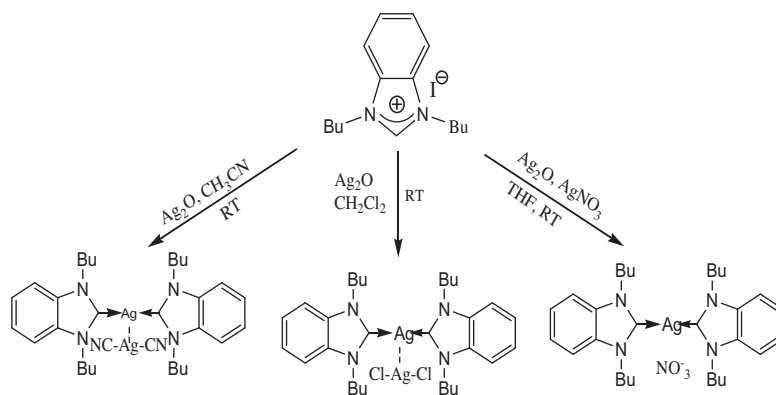
Scheme 1   Iodide/anion exchange to benzimidazolylidene silver complexes.
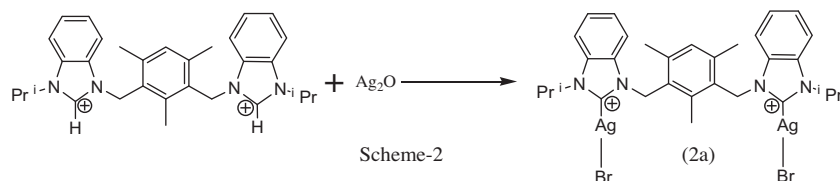
Scheme 2   Synthesis of bis-benzimidazolium salts.
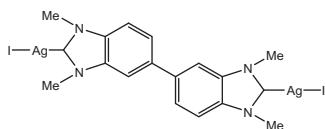
Figure 2   Tetramethylbis(benzimidazolium) diiodide complex.

for reference electrode potential measurements. Moreover, cell potential measurements involving dramatic changes in pH values of media could cause inaccurate and poor reproducibility in the measurements. To overcome the drawbacks Park et al. (2010) synthesized novel reference electrode material namely silver(I) tetramethylbis(benzimidazolium) diiodide (Fig. 2) for both acid and alkaline electrolysis. The potential usage of the silver complex as a reference electrode with at least equal electrochemical capabilities compared to those of the conventional electrode materials (e.g., Hg/HgO in alkaline media and Ag/AgCl in acidic media) are also demonstrated using cyclic voltammetry. In addition, the well dispersed surface morphology and fine crystallinity of the silver complex are investigated using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD).

2.5. Antimicrobial activity

The first Ag(I)–NHC complexes possessing antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas* aeruginosa were reported (Melaiye et al., 2004). Synthesized silver–NHC complexes Scheme 3 (**3a–f**) from the benzimidazolium salts by the reactions with Ag₂O in dichloromethane as a solvent at room temperature. Chloro[1-(2,4,6-trimethylbenzyl)-3-(methoxyethyl)benzimidazol 2-ylidene]silver(I) complex was structurally characterized by single-crystal X-ray diffraction. A series of new Ag NHC complexes were screened and determined by using agar dilution procedure recommended by the Clinical and Laboratory Standards Institute for their in vitro antimicrobial activity against a variety of Gram-positive and Gram-negative bacteria as well as for their antifungal activity against *Candida albicans* and *Candida tropicalis*.

2.6. Pastes in electronic applications

There are many applications of silver–NHC complexes as certain materials, however the use of silver(I)–NHC complexes in conductive silver pastes is not common. Because silver(I) salts and elemental silver are effective electroconductive materials used in commercial printed circuit boards (PCBs) (Wu et al., 2007; Chun et al., 2009; Zheng et al., 2003), one might expect that a silver(I)–NHC complex would boast identical or improved chemical and physical properties. Silver pastes composed of organosilver complexes, such as Ag(I)–NHCs, have electronic properties comparable to commercial Ag(I)–carboxylates and can be used in electronic devices instead of metallic nanoparticles (Kamyshny et al., 2005). Silver ink and silver
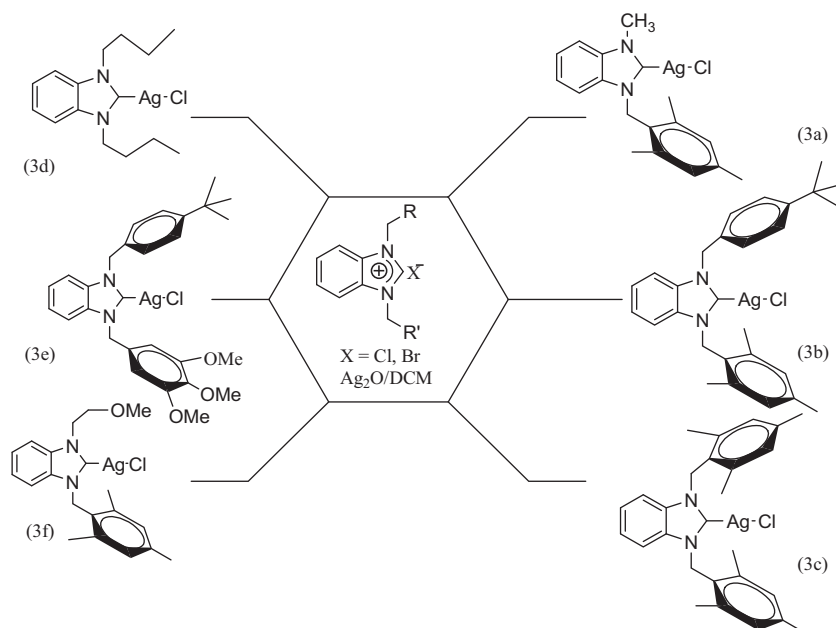
Scheme 3   Synthesis of Ag(I)–NHC complex.
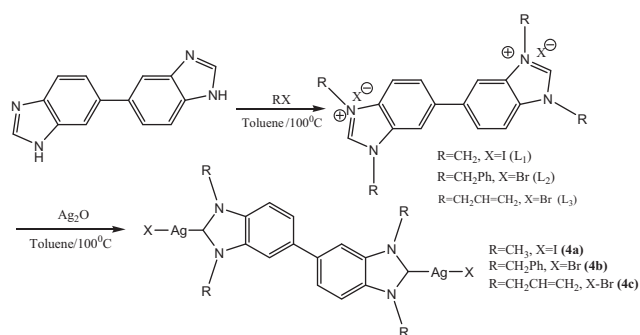
Scheme 4 Synthesis of the new Ag(I)–NHC complexes.

Scheme 5 [1,3-Di-i-propyl-benzimidazol-2-ylidene]AuCl.

pastes are commonly used in inkjet (Calvert, 2001; Lee et al., 2006) and roll printing processes to fabricate conductive patterns on substrates such as PCBs and can be applied to PDP electrodes, FPCB circuits, RFID antennas, EMI screens, solar cells and flexible displays (Valentini et al., 2008; Yiwei et al., 2007).
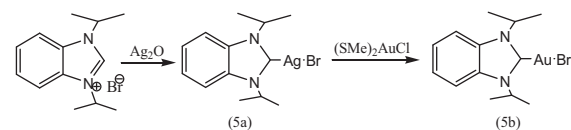
Hence the new organosilver complexes, silver(I) tetraalkyl-bis(benzimidazolidene) halide [**4a–4c**] were synthesized and incorporated (Park et al., 2011) into electroconductive silver pastes. Complex (**4c**) had a 15-fold higher conductivity than conventional silver salt pastes, specifically silver(I) hexanoate exhibited a smooth, homogeneous surface after reductive heat treatment of the silver paste. While the conductivity of silver(I) hexanoate can be increased by up to 33% by the addition of a supporting silver source, such as Ag$_2$O, the conductivity of **3a** was markedly decreased by Ag$_2$O treatment. Thus, **3a** can be used in silver pastes with moderate conductivity and can reduce the amount of conventional silver supporting materials without loss of electroconductivity (Scheme 4).

3. NHC–Au complex

The catalytic potential of gold has started to unravel, with a display of quite an impressive range of transformations emerging by the day that varies from hydroarylation, to C–C and C–O bond formations, to hydrosilylation, to hydroamination, to carbonylation of amines (Shi and He, 2004). As a consequence, gold, otherwise deemed as an unreactive coinage metal with limited utility in catalysis, has received unprecedented attention of late. Not surprisingly, riding high on the successes of N-heterocyclic carbenes (NHCs) in homogeneous catalysis, the new gold–NHC based catalysts are spearheading the developments in this field with several first claims showing up against their names and thereby underscoring the new-found role of gold in catalysis. For example, (Schneider et al., 2003) reported the first ever use of a Au–NHC complex in homogeneous catalysis in the form of the addition reaction of water to 3-hexyne, while Fructos et al. (2005) reported the first example of a Au–NHC complex for ethyl diazoacetate assisted carbene-transfer reaction.

3.1. Ring-opening polymerization of L-Lactide

Synthesis, structures and catalysis studies of gold(I) complexes of N-heterocyclic carbenes namely, a non-functionalized [1,3-di-i-propyl-benzimidazol-2-ylidene], are reported. Specifically, the gold complexes, [1,3-di-i-propyl benzimidazol-2-yli-

dene]AuCl (**5b**), were prepared (Ray et al., 2007b) from the respective silver complex **5a** by treatment with (SMe$_2$)AuCl in good yields following the commonly used silver carbene-transfer route. The silver complex (**5a**) was synthesized from the benzimidazolium halide salts by the reactions with Ag$_2$O (Scheme 5). The NHC precursors were synthesized using an epoxide ring-opening reaction by Ray et al. (2006) and Arnold et al. (2004). The complex has been structurally characterized by X-ray diffraction. The structural studies revealed that geometries around the metal centers were almost linear in these gold complexes. The gold (**5b**) complex efficiently catalyze the ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions producing polylactide polymer of moderate to low molecular weights with narrow molecular weight distributions.

3.2. Antimicrobial activity

In 1985 auranofin, an orally bioavailable, monomeric gold(I) phosphine drug was introduced for rheumatoid arthritis. Neutral [Au(NHC)L] type compounds, analogs of [Au(PEt$_3$)Cl] and auranofin, have also been discussed. The biomedical applications of metal complexes based on N-heterocyclic carbenes are just beginning to unfold, despite such complexes being phenomenally successful in homogeneous catalysis. Ray et al. (2007a) designed and utilized NHC–metal complexes such as Pd, Ag and Au as metallopharmaceuticals. Recently, Ag–NHC complexes that showed significant antimicrobial activity were reported by Hindi et al. (2009). Au–NHC complexes, although known for decades have only recently made a greater impact on NHC chemistry due to the potential applications in medicinal chemistry spanning antiarthritic, antitumor and antimicrobial activities (Hindi et al., 2009).

Ozdemir et al. (2010a,b) have presented some novel benzimidazole-2-ylidene Au(I) complexes. The antibacterial activity of the Au(NHC)Cl complexes was tested in vitro against various microbial strains. The gold complex **2** (Fig. 3) showed only antifungal activity, while **1** and **3** inhibited the growth of Gram-positive bacteria better than **2**. It was found that antimicrobial activity of the gold(I) carbene complexes against different kinds of bacteria and fungi varies with the nature of the ligand.

4. NHC–Ru complexes

4.1. Reduction of ketones

The hydrogenation of carbonyl compounds is an important reaction on both laboratory (Andersson and Munslow, 2008) and industrial scales. Considering the complexity and functional group density of common synthetic targets, efficient and chemoselective methods to affect this transformation are necessary (Ohkuma et al., 2004). Furthermore, the develop-
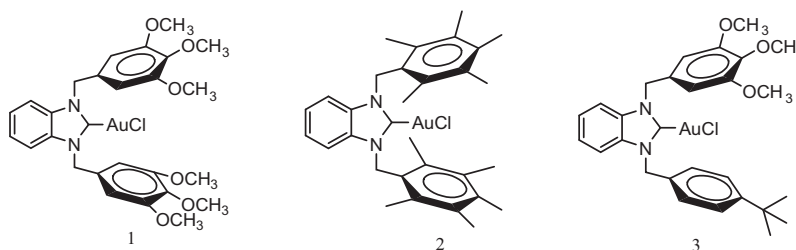
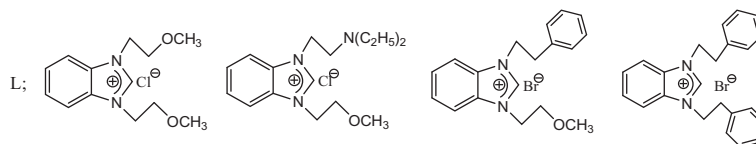**Figure 3**   Gold(I) N-heterocyclic carbene complexes.

Figure 4   1,3-Dialkylbenzimidazolium salts.

ment of enantioselective methods to affect this transformation is highly desirable. Praetorius et al. (2010) synthesized a series of $Cl_2Ru(diphosphane)L_2$ (II) complexes in which L = N^1-alkylated benzimidazoles, bonding to the metal through nitrogen and characterized. In the case of 1-methylbenzimidazole, the resulting complexes exist as statistical mixtures of all possible conformational isomers. When the size of the substituent on the benzimidazole ring was increased, complexes exist as a single diastereomer. All complexes possessing benzimidazole ligands bound to the ruthenium center are active for the mild and chemoselective hydrogenation of ketones in the presence of alkenes. Catalysts that exist as a single diastereomer, prepared with enantiomerically pure diphosphanes, catalyze the hydrogenation of prochiral ketones with moderate levels of enantioselectivity that are significantly improved relative to catalysts existing in several conformations.

4.2. Regioselective allylic alkylation and etherification

Metal-catalyzed allylic substitution is recognized as a useful process in organic synthesis for C–C and C-heteroatom bond forming reaction. N-heterocyclic carbenes (NHC) have attracted considerable attention, not only as isolable species, but also as ligands for transition-metal catalysts. Mori and co-workers have involved NHC ligands in palladium complexes to achieve allylic substitution (Sato et al., 2005). But the control of the regioselectivity is of crucial importance when unsymmetrical allylic derivatives are used as substrates.

A combination of a Cp-Ru moiety and NHC ligand allows the achievement and improvement of both catalytic activity and regioselectivity as compared to (i) Cp-(bipy)Ru precursors toward soft carbon nucleophiles and (ii) [Cp-(MeCN)$_3$-Ru][PF$_6$] toward aryl oxide anions. Among the different precursors (Fig. 4), it is difficult to select one for its better efficiency as the observed regioselectivities are quite similar and slightly depend on the nature of the nucleophile. Gurbuz et al. (2006) synthesized benzimidazolium halides which are used for the first time as ligand precursors in ruthenium-catalyzed substitution of allylic carbonates and chlorides by carbon nucleophiles and phenols, respectively. After generation of diaminocarbene species upon deprotonation by tBuOK, their
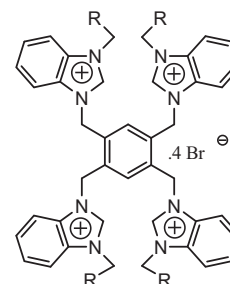
Figure 5   General formula of the tetrazolium salt.

association with [Cp-Ru(MeCN)$_3$]PF$_6$ induces a very high regioselectivity in favor of the branched isomers when cinnamyl derivatives are used as starting substrates. They also provide good regioselectivities for the allylation of phenols by unsymmetrical aliphatic allylic substrates such as 3-chloro-4-phenylbut-1-ene and thus provide a straightforward access to new allylic phenyl ethers.

4.3. Allylation reaction

The substitution of allylic substrates via allyl-metal intermediates is recognized as a powerful reaction in organic synthesis for C–C and C-heteroatom bond formation in a controlled manner. Several transition metals including Pd, Mo, Ir, Rh, W, Ni, Fe and Ru, exhibiting different specificities in terms of regioselectivity properties have been used for this purpose. (Gurbuz et al., 2010) prepared a new N-heterocyclic tetracarbene benzimidazolium bromide precursor (Fig. 5) and this new tetrabenzimidazolium salt, was symmetrically attached to a 1,2,4,5-phenyl unit and fully characterized. After deprotonation with tBuOK, the resulting species have been associated to a Ru-Cp center in order to generate catalyst precursors for nucleophilic allylic substitution of cinnamyl chloride and carbonate by amines, phenols and carbonucleophiles. All the catalytic systems are active for nucleophilic substitution of non-symmetrical allylic substrates and most of them lead to the regioselective formation of branched products.
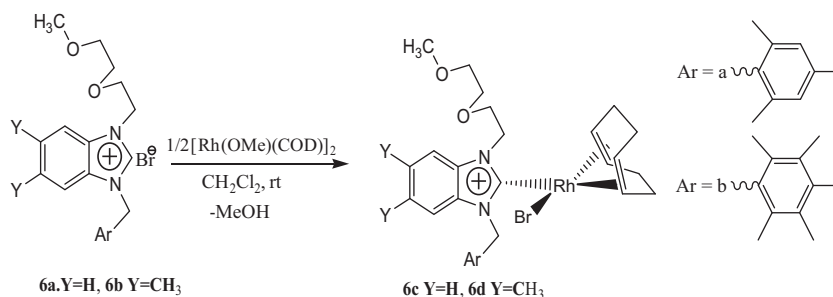
5. NHC–Rh complex

5.1. Transfer hydrogenation reactions

Transfer hydrogenation (TH) is the addition of hydrogen to an unsaturated molecule by a reagent other than H_2. Typically a sacrificial reagent (hydrogen donor) such as 2-propanol together with a strong base and Ru, Rh or Ir catalyst is used (Gnanamgari et al., 2009). NHC–rhodium complexes have been employed as catalysts for hydrogenation, transfer hydrogenation and hydrosilylation.

(Gulcemal et al., 2011) synthesized Rhodium(I)–NHC complexes (**6c** and **6d**) bearing one diether substitution on N^1 and bulky benzyl groups $(CH_2–C_6H_2(CH_3)_3$-2,4,6 and $CH_2–C_6(CH_3)_5)$ on N^3 of (5,6-dimethyl)benzimidazole by deprotonation of two equivalents of benzimidazolium salt [**6a** and **6b**] with [Rh(μ-OMe)(1,5-cod)]$_2$ in dichloromethane at ambient temperature (Scheme 6). The complexes **3** and **4** were obtained in high yields as air-stable orange solids and the identity of **6c** and **6d** as cis-complexes has been confirmed by X-ray diffraction studies.

All of these new complexes have been found to be active catalysts for transfer hydrogenation of acetophenone in 2-propanol. The complexes with a pentamethylbenzyl substituent on the N^3 atom of benzimidazole showed slightly better activities than complexes with a 2,4,6-trimethylbenzyl substituent. Electron-donating methyl groups on the 5,6-positions of benzimidazole also increase the catalytic activity. However, introduction of second ether functionality on the methoxyethyl substituent on N^1 atom does not improve the activity.

6. NHC–Fe complex

6.1. Heck reaction and antifungal agents

The azole system arguably represents one of the most ubiquitous classes of heterocyclic species. Their many wide-ranging applications vary from medicinal use as pharmaceuticals to being some of the building blocks necessary for life. The application and derivatization of azolium salts focused on their ability to act as potential anion receptors and their biological activity (Howarth and Al-Hashimy, 2001; Howarth and Hanlon, 2003). Dallas et al. (2007) reported a new series of acyclic and cyclic ferrocenyl azole/azolium compounds based on benzimidazole (Scheme 7). These compounds successfully aided the catalysis of Heck reaction with the product being formed in very high yields in some cases. This result adds to the growing, albeit still small, evidence of benzimidazolium salts acting as effective ligands in such reactions and their application as auxiliary ligands in transition-metal catalysis, anion receptors and bioactive agent.

6.2. Magnetic property and electrocatalysis

ILs [bmim]/[Fe(II)/Fe(III)-Cl$_n$] were studied by Raman spectroscopy. Tilve et al. (2004) studied the successful role of [bmim]Cl–FeCl$_3$ system as a solvent and a catalyst in the stereocontrolled glycosidation of 3,4,6-tri-O-acetyl-D-glucal with different alcohols. (Sun et al., 2004) demonstrated the use of [bmim]Cl–FeCl$_3$ system for the alkylation of deuterated benzene with ethylene. Kolle and Dronskowski (2004) prepared

Scheme 6   Synthesis of rhodium(I)–NHC complexes.
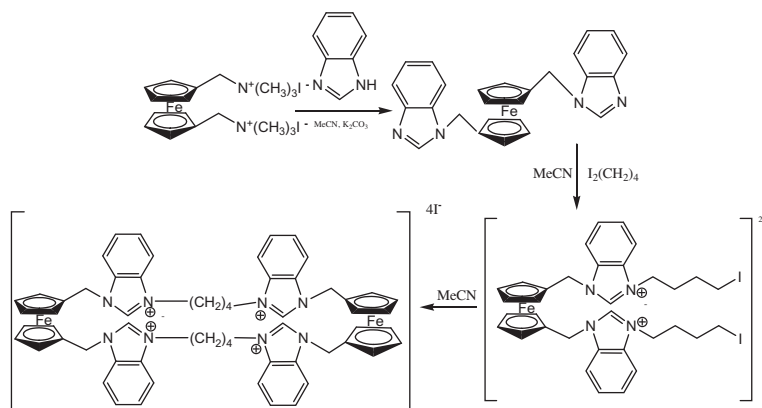
Scheme 7   Synthetic strategy to introduce from azolium centers for the preparation of cyclophane.

the ILs composed of chloroferrate(II, III) and investigated the role of hydrogen bonding on the lattice energies. Several Fe-containing ionic liquids have been prepared and reported to show a strong response to magnetic fields (Lee and Ha, 2007). In addition, Nguyen's group reported Fe-containing ionic liquids as catalysts for the dimerization of bicyclo [2.2.1] hepta-2,5-diene, which showed that Fe(II) was the active species for the dimerization.

Many substrates such as porphyrins and heteropolyanion systems have been used for the electrocatalytic reduction of nitrite in the past (Wang et al., 2008). Wang et al. (2011) synthesized a metal-containing ionic liquid [(C4H9)$_2$-bim]FeCl$_4$ and its structure was characterized. In the crystal packing, the benzimidazolium cations form one-dimensional channels, and in each channel, the [FeCl$_4$]-anions are packed in a line and fixed in the center of the channel through hydrogen bonds. The DSC analysis and TG/DTG of Fe-IL showed the thermal stability in wide temperature range. The value of magnetic moment and its temperature dependence indicates that Fe-IL is paramagnetic. The Fe-IL/CPE showed excellent electrocatalytic activities toward the reduction of nitrite and bromate and the results were reproducible with a lower detection limit which is important for practical application on electrochemical sensors.

7. NHC–Co complex

7.1. Supporting electrolyte

The presence of metal ions in ILCs provides many additional properties such as color, geometry and magnetism. These properties cannot be achieved easily by conventional ILCs. Metal-containing ILCs are potentially very useful as ordered media, catalysts and catalyst precursors for chemical transformations (Lee et al., 2004). A new cobalt-containing ionic liquid crystal of N,N'-dialkylbenzimidazolium of [(C$_{12}$H$_{25}$)$_2$-bim]$_2$-[Co(SCN)$_4$] was synthesized by Wang et al. (2011) with reaction of the ligand [(C$_{12}$H$_{25}$)$_2$-bim]Br and cobalt (II) thiocyanate. Its structure was characterized by X-ray crystallography, IR spectroscopy and elemental analysis. The cation of the title complex adopts a U-shaped conformation and is packed in a highly interdigitated bilayer fashion. The distorted tetrahedron [Co(SCN)$_4$]$^{2-}$ is located between the cationic bilayers individually. The liquid crystalline behavior of the title complex was studied by differential scanning calorimetry and polarized optical microscopy. The results of the ionic conductivity measurement displayed that the ionic conductivity of the complex was significantly higher than that of the ligand. The conductivity of the complex had very large difference in different organic solvents, while that had a maximum value in N,N'-dimethylformamide solution.

8. NHC–Cu complex

8.1. Aldol condensation

The development of mild, catalytic and enantioselective versions of fundamental C–C bond forming processes is a topic of paramount importance in modern organic chemistry. Arnold et al. (2004) as well as Hénon et al. (2008) independently introduced chelating alkoxy NHC–Cu complexes for
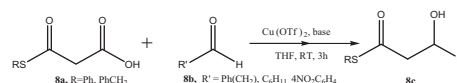
Scheme 8 Synthesis of aldol adducts from thioesters and aldehydes.

asymmetric alkylation. In this context, the aldol reaction continues to attract a great deal of interest. Very recently, the decarboxylative condensation between S-benzylmalonic acid hemithioester and aldehydes catalyzed by a combination of Cu(2-ethylhexanoate) (20 mol%) and 5-methoxybenzimidazole (22 mol%) has been described as a new protocol to perform an aldol process under exceptionally mild conditions (wet solvent, air, room temperature), reminiscent of those typical of polyketide biosynthesis.

Orlandi et al. (2004) introduced the condensation between S-phenylthioester (**8a**) (1 mol equiv) and 3-phenylpropanal (**8b**) (1 mol equiv) carried out in the presence of 20 mol% of various Cu(II) salts and 22 mol% of chiral imidazoles to afford aldol adduct (**8c**) (THF, 3 h, room temperature) which was used as a model reaction (Scheme 8).

A catalytic, enantioselective version of a very mild aldol condensation process has been developed. The reaction relies on the unprecedented use of a combination of 20 mol% each of a Cu(II) salt, an achiral base and a readily available and inexpensive tartaric acid-derived enantiopure bisbenzimidazole.

8.2. Alkylation of enone

The conjugate addition (1,4-addition) of carbon nucleophiles to α,β-unsaturated carbonyl compounds is one of the most widely used methods for the construction of C–C bonds. Over the past decade, much attention has been paid to the enantioselective conjugate addition (ECA) reaction catalyzed by a copper salt combined with a functionalized NHC. In 2001, Alexakis and Roland independently reported that monodentate Arduengo-type diaminocarbene ligands afforded moderate enantioselectivity in the 1,4-addition of Et$_2$Zn to cyclic enones (Pytkowicz et al., 2001). The introduction of a second coordination site at the NHC ligand provided a tightly coordinating polydentate NHC ligand system that is expected to enhance catalyst stability. Pioneering work was performed (Arnold et al., 2004) in which the Cu-catalyzed enantioselective conjugate addition reaction proceeded with moderate enantioselectivity using a chiral anionic tethered bidentate NHC ligand. A breakthrough was achieved by Mauduit and Alexakis who developed various bidentate hydroxyalkyl-NHC precursors for the ECA reaction of cyclic enones with dialkylzincs as well as the 1,4-addition reaction of β-substituted cyclic enones with Grignard reagents (Wencel et al., 2009). Moreover, Lee et al. (2009) introduced chelating anionic hydroxyaryl-NHC ligands which were successfully used not only in asymmetric catalytic allylic alkylations but also in ECA reactions.

Harano and Sakaguchi (2011) have demonstrated that a C$_2$-symmetric bis(hydroxyamide)-functionalized benzimidazolium salt efficiently performs a copper catalyzed asymmetric conjugate addition of dialkylzinc reagents to cyclic enones (Scheme 9) with up to 96% ee. These air-stable, chiral ligands are especially useful because of the operational simplicity of
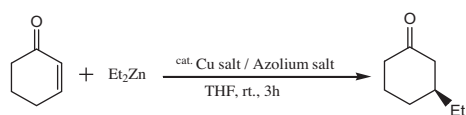
Scheme 9 ECA reaction of **6** with Et$_2$Zn catalyzed by Cu salt combined with benzimidazolium salt.
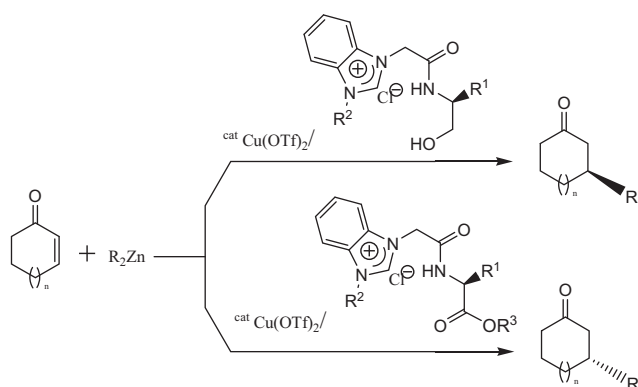
Scheme 10 Strategy for switching of enantioselectivity.

their preparation. In addition, the ECA reaction could be carried out at ambient temperature without controlling the temperature of the solution.

Yoshimura et al. (2011) reported a series of ester/amide-functionalized azolium compounds derived from natural α-aminoesters for use as chiral NHC precursors for a Cu-catalyzed ECA reaction. The reaction of cyclic enones with dialkylzincs catalyzed by Cu(OTf)$_2$ combined with the appropriate chiral azolium salt derived from an (S)-serine ester gave the corresponding optically active conjugate adducts with moderate to excellent enantioselectivities (69–97% ee) (Scheme 10). In contrast, the use of the hydroxy-amide-functionalized azolium salt derived from β-amino alcohol led to the formation of adducts with opposite configurations with 82% to >99% ee. The preparation of both enantiomers of a chiral compound is increasingly important not only in life science, including medicine and agricultural chemicals, but also in material science.

9. NHC–Cd complexes

9.1. Electrocatalytic activities

Cadmium(II) containing ionic liquid [(C$_{10}$H$_{21}$)$_2$-bim]$_2$[Cd$_2$Cl$_6$] was synthesized by Zhuang et al. (2009). The electrochemical behavior and electrocatalysis of the Cd-IL/Carbon paste electrode (CPE) had been investigated having double function of a binder and an electrocatalyst. This modified electrode showed excellent electrocatalytic activities toward the reduction of hydrogen peroxide and bromate. Peroxide hydrogen is the product of the reactions catalyzed by a large number of oxidases and it is essential in food, pharmaceutical and environmental analyses. The detection limit is 0.2–1.5 μM for hydrogen peroxide. The results were reproducible with a lower detection limit, which was suitable for the quantitative analysis of environmentally hazardous materials.
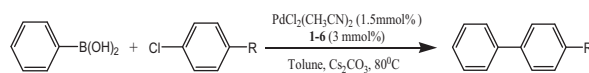
Scheme 11 Suzuki coupling of aryl chlorides with phenylboronic acid.

Zhuang et al. (2010) extended his work by synthesizing a new ionic liquid [(C$_3$H$_7$)$_2$-bim]$_2$[CdCl$_4$]. The Cd-IL/CPE has good electrocatalytic activity in the reduction of trichloro acetic acid (TCA) and bromate. The detection limit and the sensitivity are 0.01 μM and 102.72 μA μM^{-1} for trichloroacetic acid while 0.003 μM and 496.15 μA μM^{-1} for bromated detection. The advantages of the Cd-IL/CPE are its stability, excellent catalytic activity, low detection limit and simplicity of preparation in comparison with the other methods.

10. NHC–Pd complex

Palladium catalysts have become fundamental tools for a number of organic reactions. In the last decade, the following three topics have attracted much attention: (i) minimizing the relative amount of the metal-containing catalyst, (ii) its recovery and recycling and (iii) the employment of environmentally more friendly methodologies.

10.1. Suzuki coupling

Biaryls constitute important building blocks for the synthesis of biologically active substances, e.g. pharmaceuticals and herbicides (Yasuda, 2002). Palladium-catalyzed cross-coupling reaction between aryl halides or triflates and organometallic reagents (Sn, Mg, B, Li, Zn, etc.) has been developed as a versatile and efficient method for a variety of synthetic transformations.

The catalysts were prepared in situ by Ozdemir and coworkers from PdCl$_2$(CH$_3$CN)$_2$ and the appropriate 1-alkylbenzimidazole in the toluene. The Pd-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions. Under those conditions, p-chlorobenzene, p-chlorotoluene, p-chlorobenzaldehyde, p-chloroacetophenone and p-chloroanisole react very cleanly with phenylboronic acid in good yields (Scheme 11). These novel palladium/1-alkylbenzimidazole catalyst systems (Wen et al., 2005) were found to be active for Suzuki reactions in toluene, giving quantitative yields for p-chloroarenes. A good yield was achieved for the activated p-chloroacetophenone, although no significant amounts of coupling were observed for other chloroarenes. These new benzimidazole ligands allow highly efficient coupling reactions of electron rich as well as electron poor aryl chlorides with phenylboronic acid under mild conditions.

Wen et al. (2005) introduced five representative benzimidazolium salts that have been studied in constructing palladium catalyst systems for the Suzuki coupling, from which a practical and highly active palladium catalyst system has been developed from the simplest palladium source PdCl$_2$ and readily available N,N′-dibenzylbenzimidazolium chloride. A different substituent effect has been uncovered with respect to nitrogen substituents of benzimidazolium salts from the imidazolium salt analogs. The PdCl$_2$ catalyst system has proven to be highly efficient for the coupling of a wide array of
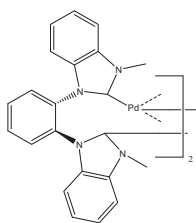
Figure 6 NHC Pd(II) complex.
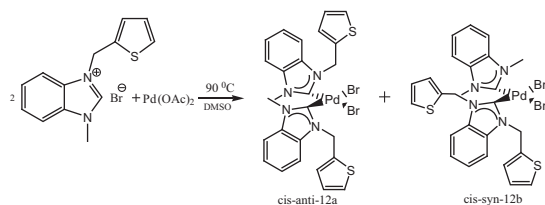
Scheme 12 Preparation of Pd(II)bis (carbene) complex cis-**12a** and **12b**.

aromatic halides including chlorides with arylboronic acids. The effective palladium loading could be as low as 0.0001 mol% and 0.01–0.1 mol% for iodide and bromide substrates, respectively. The coupling of aromatic chlorides with arylboronic acids also gave good results using the PdCl$_2$ catalyst system with 2 mol% palladium loading and Cs$_2$CO$_3$ as the base. Electron-deficient aromatic halides reacted faster and gave higher yields than the electron-rich ones, indicating that the electronic factor from aromatic halides exerted a significant influence on the Suzuki coupling catalyzed by the palladium–benzimidazolium system while the electronic effect from the arylboronic counterparts is almost negligible. These results suggest that the N-heterocyclic carbenes from benzimidazolium salts are promising ligands for the homogenous transition-metal catalysts.

Shi and Qian (2005) examined the Suzuki–Miyaura cross-coupling reaction of aryl chlorides with phenylboronic acid using novel dimeric bidentated NHC–Pd(II) complex and KO, but as a base in DMA (Fig. 6). Previously, Nolan et al. reported that using alcohols as solvent, the reaction could be achieved at room temperature in the presence of NaOtBu (Navarro et al., 2003). Therefore, they examined the additive effects of iso-propanol and tert-amyl alcohol (1.5 mL) on this type of Suzuki–Miyaura cross-coupling reaction with 55% yield under identical conditions. For two other aryl chlorides such as 4-methylphenylchloride and 4-acetylphenylchloride, the corresponding coupled products were obtained in 45% and 62% yields, respectively.

10.2. Suzuki–Miyaura cross-coupling

Pd complexes of unsaturated imidazolin-2-ylidenes and saturated imidazolidin-2-ylidenes have been developed as highly

reactive precatalysts in C–C and C–N coupling reactions (Hahn, 2006). Catalytic applications of benzannulated carbenes have received less attention, although this class of carbenes occupies an interesting intermediate position between the former two and thus exhibits unique properties. Yuan et al. (2008) reported that reaction of the sterically bulky 1,3-dibenzhydrylbenzimidazolium bromide (Bh$_2$bimyH$^+$Br$^-$) (A) with Pd(OAc)$_2$ in DMSO yielded a mono(carbene) Pd(II) complex **1** with a N-bound benzimidazole derivative, which resulted from an unusual NHC rearrangement reaction. Reaction of A with Ag$_2$O, on the other hand, cleanly gave the Ag(I) carbene complex [AgBr(Bh$_2$-bimy)] (**2**), which has been used as a carbene-transfer agent to prepare the acetonitrile complex trans-[PdBr$_2$(CH$_3$CN)(Bh$_2$-bimy)] (**3**). Dissociation of acetonitrile from complex **3** and subsequent dimerization afforded the dinuclear Pd(II) complex [PdBr$_2$(Bh$_2$-bimy)]$_2$ (**4**) in quantitative yield. Furthermore, the catalytic activity of complex **4** in aqueous Suzuki–Miyaura cross-coupling reactions was studied and compared with that of its previously reported less bulky analog [PdBr$_2$(iPr$_2$-bimy)]$_2$.

10.3. Heck coupling

Suleyman et al. (2011) reported that the dimeric Pd(II) carbene complexes of N^1-oligoether-substituted (5,6-dimethyl)benzimidazole-2-ylidenes were obtained in about 80% yield in halogenated solvents. These complexes are useful precursors for the preparation of neutral and mixed NHC–phosphine complexes of Pd(II) under mild conditions and were tested as catalyst for the Heck coupling reaction in water. The influence of oligoether and benzyl substituents on N atoms and CH$_3$-substituents on the 5,6-positions of benzimidazole frame were investigated under the same conditions in the Heck coupling reaction. In situ formed catalysts showed better conversions than the isolated Pd (II) complexes. The length of the oligoether spacer significantly increases the activity.

N-functionalization with N-, O- and P-donor groups is relatively common, whereas carbene ligands bearing softer sulfur-donors are surprisingly rare, although some thiolate–NHCs, thioether–NHCs and thiophene–NHCs (McGuinness et al., 2008) have been reported. Huynh and Chew (2010) reported the facile synthesis of a new palladium(II) complex bearing two unsymmetrical, thienylmethyl functionalized benzimidazolin-2-ylidene ligands. A preliminary catalytic study shows that the complex (**12a** and **12b**) (Scheme 12) is highly active in the Suzuki–Miyaura coupling of activated and deactivated aryl bromides in/on water as green reaction media.

Heck reaction was also examined in DMA by Shi and Qian (2005). The reaction of bromobenzene with butyl acrylate in the presence of various bases and additives showed that K$_2$CO$_3$ afforded the best results for this reaction and allowed the coupling product (Scheme 13) to be obtained in 80% under ambient atmosphere at 160 °C in the presence of C$_{16}$H$_{33}$Me$_3$NBr (1.0 mol%).
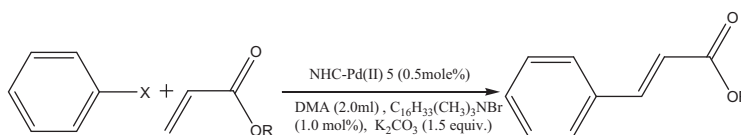
Scheme 13 Palladium-catalyzed C–C coupling reaction of alkyl acrylate with aryl halides.
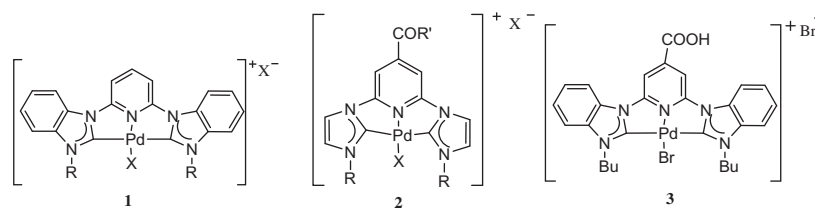
Figure 7   Pyridine-bridged palladium pincer complexes.
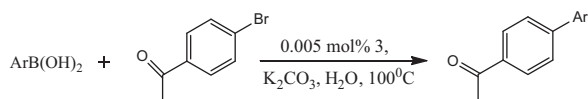
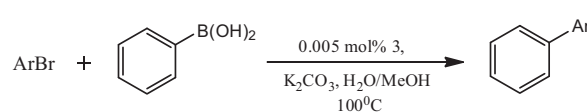**Scheme 14**   Suzuki–Miyaura coupling of 4-bromoacetophenone with aryl boronic acids catalyzed by palladium princer complex **3** in water.

Scheme 15   Suzuki–Miyaura coupling of aryl bromides with phenyl boronic acid catalyzed by palladium princer complex **3** in aqueous solvents.

Recently, Tao et al. (2010) reported that pyridine-bridged palladium pincer complexes (**1**) (Fig. 7) and their precursors not only functionalized as efficient gelators for a variety of organic solvents and ionic liquids in extremely low gelator concentration and showed potential applications in gel catalysis and solar cells (Tu et al., 2008, 2009) but also demonstrated their powerful catalytic activities in homogenous C–C couplings even with catalyst loadings down to the ppm scale. Firstly we explored the catalytic role of complex (**3**) in the Suzuki–Miyaura couplings in aqueous conditions.

Inspired by these attractive results of various arylboronic acids, the influences of electronic and steric properties of electrophiles were next tested with a variety of (hetero)-bromoarenes. The best results were found in the coupling of phenyl boronic acid with bromobenzene when the ratio of H_2O–MeOH is in 1:1 ratio.

A robust hydrophilic pyridine-bridged bisbenzimidazolylidene pincer palladium complex **3** (Fig. 7), which is readily accessible from inexpensive and commercial precursors, demonstrated excellent catalytic activity toward Suzuki–Miyaura coupling reactions (Schemes 14 and 15) As a practical and environmentally-friendly protocol, the products could be easily separated after reaction by simple filtration and the filtrate could be reused as a catalyst several times. In contrast to imdazolium analogs, the palladium pincer complex (**3**) acts as a molecular catalyst, which may be attributed to the steady Pd–C imposed by the stronger s-donating property of benzimidazolylidene compared to imidazolylidene and hardly broken to form Pd nanoparticles during the reaction process.

In the last decade, heteroatomic neutral or an anionic chelate ligand incorporated in NHC–metal complexes having stereodirecting groups. For the neutral-functionalized NHC, a breakthrough has been achieved by Burgess, who reports highly efficient asymmetric hydrogenation catalysis based on carbene/oxazoline iridium complexes (Nanchen and Pfaltz, 2006). Other important chiral bidentate NHC complexes have been developed by Gade et al. (2004) and Douthwaite (2007) for enantioselective hydrosilylation and alkylation, respectively.

Recently, Sakaguchi et al. (2010) developed a novel chiral tridentate NHC–ligand and their Pd(II) complexes (Fig. 8). Importantly, the Pd(II) complex derived from chiral β-amino
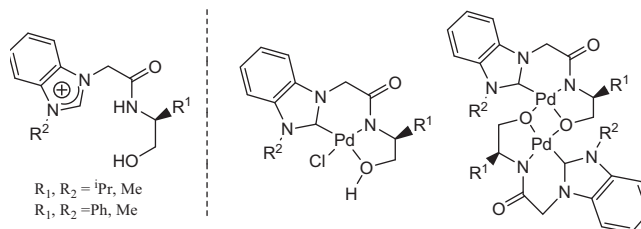

Figure 8   Benzimidazolium iodides and their Pd(II) complexes.

alcohol catalyzes an asymmetric oxidative Heck-type reaction with excellent enantioselectivity (up to 98% ee). However, only two kinds of ligands which are derived from (S)-valinol and (S)-2-phenylglycinol have been reported.

Satoshi Sakaguchi et al. have synthesized NHC-ligand precursors, azolium iodides, successfully and tried to introduce several N-alkyl groups instead of N-methyl group into the NHC proligand. However, it is more difficult to alkylate with ethyl iodide than CH_3I. Therefore, they proposed another synthetic route to the NHC proligand (Scheme 16). Reaction of chloroacetyl chloride with β-amino alcohol afforded α-chloroacetamide in almost quantitative yield, which subsequently coupled with N-alkylated azole to yield the corresponding azolium chloride. Thus, a variety of the NHC–Pd complexes could be obtained from benzimidazolium salt.

Recently, a novel family of C_2-symmetric bidentate NHCs with dihydroethanoanthracene unit has been reported by Jeletic et al. (2010). Although two NHCs in these ligands are located in cis position, the complex showed C_1-symmetric structure. Moreover Anezaki et al. synthesized a new o-xylylene-linked bis(benzimidazolium) salts in six-steps from C_2-symmetric chiral 1,4-diol, 1,2-bis(1-hydroxypropyl)benzene, as a starting material. The silver complex of bis(benzimidazol-2-ylidene) was obtained on treatment of bis(benzimidazolium) salt with silver oxide. The reaction of the silver bis-NHC with $[PdCl_2(PhCN)_2]$ afforded the bis-NHC complex of palladium. The variable temperature NMR spectroscopy revealed that these Pd complexes showed a fluxional behavior between C_1- and C_2-symmetric structures in solution state (Scheme 17).
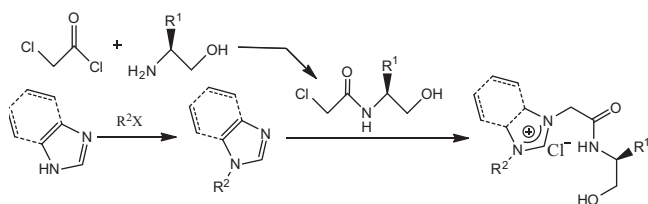
Scheme 16 Synthesis of azolium chloride.

10.4. Arylation of benzothiazole

The arylation reaction of thiazoles has been studied by Miura and Nomura. They have described that the palladium catalyzed direct arylation of thiazole with aryl bromides in DMF (Yokooji et al., 2003). Ozdemir et al. (2005) describe the successful reactions of substituted bromobenzene derivatives with benzothiazole. The influence of various organic and inorganic bases such as K_3PO_4, Cs_2CO_3, KOtBu and K_2CO_3 was studied for the standard reaction. It is observed the yield is low, hence their research group demonstrated how to produce higher

yields for the Pd–NHC catalyzed direct arylation of benzothiazole. Hence we designed and synthesized a novel air-stable palladium–N-heterocyclic carbene complex (Scheme 18). The molecular and crystal structure of the palladium complex was elucidated. The complex is found to exhibit good catalytic activity in the direct arylation of benzothiazole with arylbromides with comparable yield.

Earlier Demir et al. (2011) focused on bis(benzimidazolium) salts as NHC precursors to increase the product yield by treatment of 1-substitued benzimidazoles with 1,4-dibromobutane according to the literature (Gurbuz et al., 2006). Palladium complexes were prepared from the corresponding bis(benzimidazolium) salts and palladium acetate using well-established literature methods (Dogan et al., 2009).

Bis(NHC)–Pd complexes (**19a–d**) (Scheme 19) were synthesized and characterized. The reaction of $Pd(OAc)_2$ and a bis(benzimidazolium) salt gave the monomeric palladium complex in which the N-heterocyclic carbene was bound to the metal center, as confirmed by a single-crystal X-ray diffraction study. A simple and efficient method for the arylation of benzothiazole using bis(NHC)–Pd complexes as a catalyst was
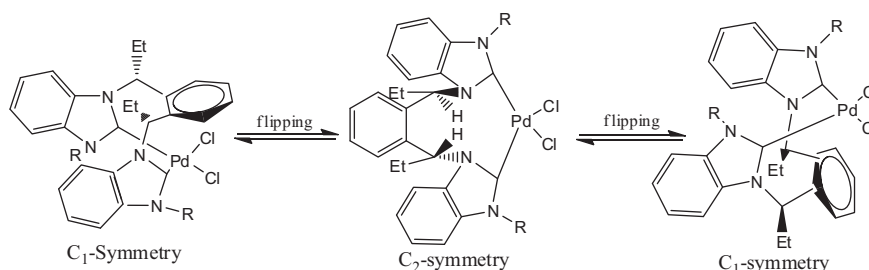
Scheme 17 Flipping motion of *o*-xylylene unit.
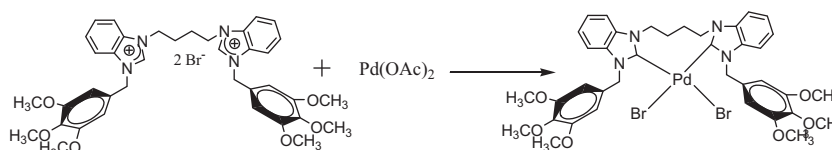
Scheme 18 Synthesis of palladium–NHC complex.
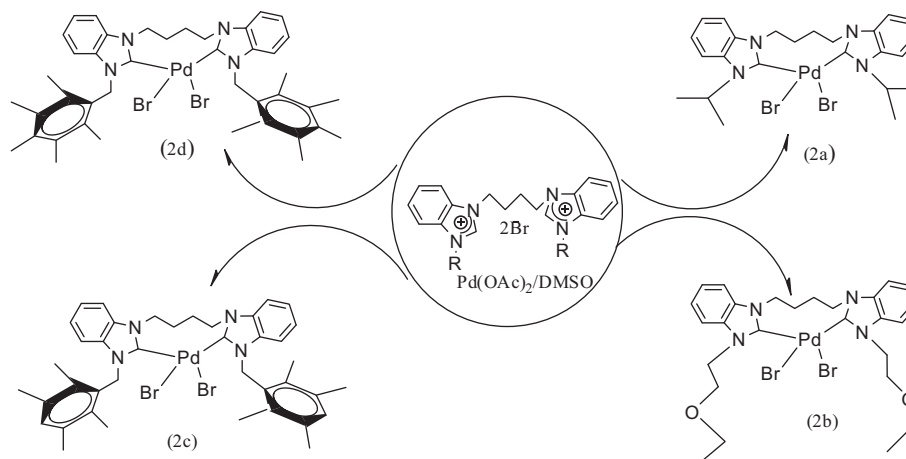
Scheme 19 Synthesis of butylene bridged palladium(II) NHC complexes.

developed which showed good catalytic activity under even milder reaction condition.

11. Conclusion

The chemistry of NHC–metal ionic liquids and their crystals based on benzimidazolium moiety is incredibly exciting in its developmental stages. The series of NHC–metal benzimidazolium salts that have been synthesized by various scientists are introduced in this review. On the basis of all the NHC of metals based on benzimidazolium ionic liquid, a lot of reactions that have been investigated like alkylation, allylation, hydrogenation, etherification, arylation etc. have the potential of these ionic liquids. The solvent environment that is provided by benzimidazolium ionic liquid is quite unlike any other available at or close to room temperature and it has a remarkable difference between the reaction in ILS and molecular solvent like hydrocarbons. It showed an eco-friendly catalyst with various transition metals in coupling reactions like Suzuki, Miyaura, Heck and aldol condensation reaction. Also it gave notable activity as phase transfer catalyst, paste in electronic application, reference electrode, supporting electrolyte, RPO of L-lactide, electrocatalyst, magnetic property, antifungal and antimicrobial activity. This is the review of NHC–metal functionalized ionic liquid based on benzimidazolium cation, we hope that this review has in some way updated that work and look forward with excitement to next.

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