Reviews

Nickel and palladium *N*-heterocyclic carbene complexes. Synthesis and application in cross-coupling reactions*

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N-Heterocyclic carbenes (NHCs) are widely used as ligands in catalysis by transition metal complexes. The catalytic activity of transition metal NHC complexes is much higher than that of the transition metal complexes bearing the phosphine and nitrogen-containing ligands. They show excellent catalytic performance in different transformations of the organic compounds, especially in the carbon—carbon and carbon—element bond forming reactions. Palladium NHC complexes are very efficient catalysts for the cross-coupling reactions. On the other hand, nickel is less expensive and regarded as a promising alternative to palladium and, therefore, it attracts increasing attention from the researches. The present review is focused on the recent advances in the synthesis of *N*-heterocyclic carbene complexes of nickel and palladium and their application in catalysis of cross-coupling reactions of organic, organoelement and organometallic compounds with organic halides.

Key words: *N*-heterocyclic carbenes, nickel and palladium complexes, homogeneous catalysis, cross-coupling reactions.

Introduction

N-Heterocyclic carbenes (NHCs) closely resemble electron-rich phosphines (PR_3). These carbenes show low toxicity and pronounced σ donating properties easily tunable by varying the substituents at the nitrogen atom, and known to exert electronic and steric effects. Due to these unique properties, NHCs are versatile and indispensable class of ligands applied in coordination chemistry and homogeneous catalysis by transition metal complexes. Transition metal NHC complexes gain increasing importance in materials sciences, medicine, and, especially, catalysis.[1—3] The most extensively studied reactions

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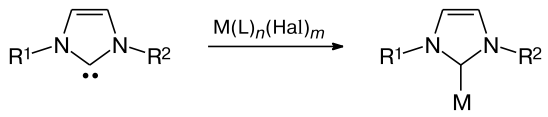
catalyzed by NHC palladium complexes are the carbon—carbon and element—carbon bond forming reactions. It is of note that at present there is a growing interest in nickel as a cheaper and promising analog of palladium. Thus, it was recently shown that some NHC complexes of nickel efficiently catalyze a wide variety of chemical transformations, *e.g.*, the Suzuki—Miyaura,[4—8] Kumada—Corriu,[9,10] Negishi,[11] and other cross-coupling reactions.

In the present review, the synthetic approaches to NHC complexes of palladium and nickel are summarized and their catalytic performance in a variety of the cross-coupling and homocoupling reactions occurring under homogeneous catalysis conditions are compared.

1. Synthesis of palladium and nickel complexes with *N*-heterocyclic carbene ligands

A number of synthetic approaches to access palladium and nickel complexes of *N*-heterocyclic carbenes are developed.[12,13] One of the most popular methods for synthesizing palladium and nickel NHC complexes is the nucleophilic reaction of free carbenes with the corresponding metal precursors (Scheme 1).[14—18] Note that strong bases (*e.g.*, potassium *tert*-butylate (Bu^tOK)) are mainly required to generate the intermediate free carbenes. The formed free carbene species are unstable.

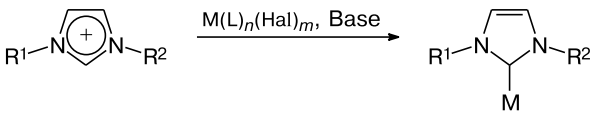
Scheme 1



R^1 and R^2 are alkyl or aryl groups, $M(L)_n(Hal)_m$ is the precursor of metal M bearing the ligand L and halogen atom Hal.

Another widely used approach towards palladium and nickel NHC complexes is an *in situ* deprotonation of the imidazolium salts in the presence of the corresponding metal precursor and base (K_2CO_3, NEt_3, *etc.*) (Scheme 2).[19—21]

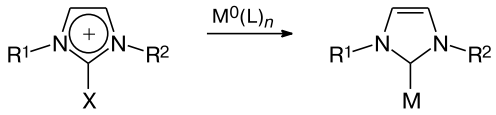
Scheme 2



R^1 and R^2 are alkyl or aryl groups, $M(L)_n(Hal)_m$ is the precursor of metal M bearing the ligand L and halogen atom Hal.

N-Heterocyclic carbene metal complexes could be also synthesized *via* the oxidative addition of the imidazolium salt bearing either H, Cl or I substituents to the corresponding metal center in a low oxidation state (Scheme 3).[22—26] The disadvantage of this method is very high moisture sensitivity of complexes of nickel(0) and palladium(0).

Scheme 3

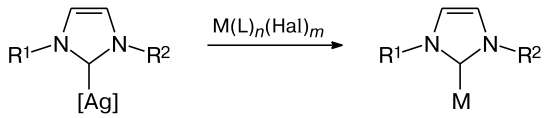


X = H, Cl, I

R^1 and R^2 are alkyl or aryl group, $M^0(L)_n$ is the corresponding precursor of metal M bearing the ligand L.

Transfer of *N*-heterocyclic carbene ligand from one metal center to another (transmetallation) is more interesting practical approach than the above-described methods. It tolerates a wide variety of imidazolium salts bearing different substituents at the nitrogen atom (Scheme 4).[27] Thus, for instance, *N*-heterocyclic carbene complex of silver(I) is the most popular reagent for transmetallation. A series of NHC nickel and palladium complexes were synthesized *via* NHC ligand exchange involving silver(I) complexes.[28—31] Note that NHC silver(I) complexes are light sensitive and unstable.[32]

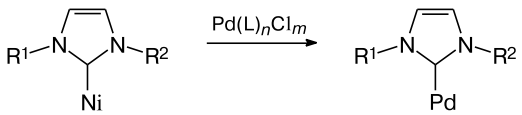
Scheme 4



R^1 and R^2 are alkyl or aryl groups, $M(L)_n(Hal)_m$ is the precursor of metal M bearing the ligand L and halogen atom Hal.

Synthesis of NHC palladium complexes involves transmetallation using NHC nickel complexes as the starting material (Scheme 5).[33]

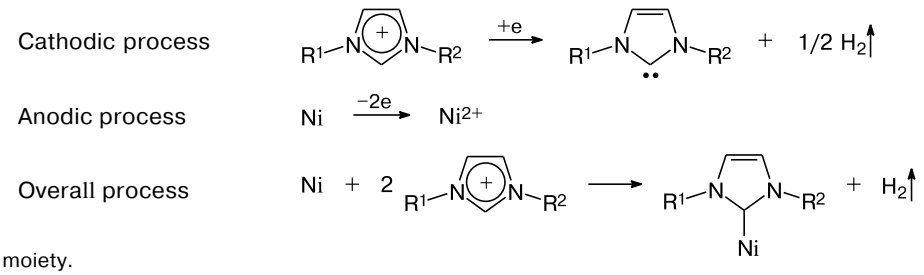
Scheme 5



R^1 and R^2 are alkyl or aryl moiety, $Pd(L)_n(Hal)_m$ is the palladium precursor bearing ligand L.

N-Heterocyclic carbene complexes of nickel were prepared by Chen and co-workers by electrolysis of imidazolium salts using the sacrificial metal anodes (Scheme 6).[34] The advantages of the electrochemical synthesis are room temperature and the use of metal plate as a metal precursor instead of the nickel complexes. Moreover, the elec-

Scheme 6



R^1 and R^2 are alkyl or aryl moiety.

trochemical procedure needs a shorter reaction time (~2 h) than the traditional chemical reactions. The reactions are mainly carried out in acetonitrile; the imidazolium salt plays a role of both *N*-heterocyclic carbene source and electrolyte. In some cases, hydrogen evolution occurs as a side process.

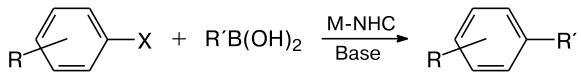
The above-described approaches were used for synthesizing a wide variety of NHC complexes of nickel and palladium. The obtained NHC metal complexes have variable properties. Thus, the valence of the metal center takes the values from 0 to +2. The nature of these complexes ranges from neutral to ionic, the carbene ligands could form mono-, bis-, tris-, and tetrakis- as well as chelate complexes. Finally, the complexes comprise different number of NHC ligands and metal centers (mono-, di, and polynuclear complexes), *etc*. Various complexes of nickel and palladium have been thoroughly reviewed.[12,13]

2. Application of nickel and palladium complexes with *N*-heterocyclic carbene ligands in homogeneous catalysis

Catalytic applications of NHC metal complexes are well studied. The NHC metal complexes are often used to catalyze hydrosilylation reactions,[12,35] redox reactions,[12,36] oligomerization and polymerization of unsaturated compounds,[12,36] *etc*. In the present review, only some applications of NHC nickel and palladium complexes in catalysis are considered. Among those are coupling reactions resulting in the carbon—carbon and carbon—element bond formation.

Suzuki—Miyaura cross-coupling. One of the most important catalytic applications of *N*-heterocyclic carbene nickel and palladium complexes is the Suzuki—Miyaura cross-coupling (Scheme 7). This cross-coupling of organoboron compounds with aryl halides is of special interest due to commercial availability and resistance towards moisture and air of the majority of the organoboron reagents.[37—39] This reaction tolerates compounds bearing different functional groups. Aryl iodides and aryl bromides are very reactive in the Suzuki—Miyaura cross-coupling, activated aryl chlorides can be also involved in cross-coupling with aryl boronic acids in the presence of bases. In the review by Prakasham and Ghosh,[12] a reference was made to the application of aryl fluorides in the Suzuki—Miyaura cross-coupling under catalysis with nickel NHC complexes. The Suzuki—Miyaura cross-coupling results in diaryls.

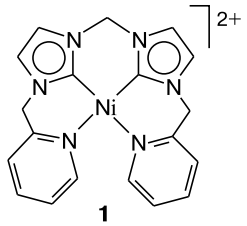
Scheme 7



X = F, Br, Cl, I; M = Ni, Pd

Palladium complexes, including palladium NHC complexes, are traditionally used to catalyze the Suzuki—Miyaura cross-coupling reactions.[40—50] Cavell and co-workers were the first to apply nickel NHC complexes to catalyze the Suzuki cross-coupling in 1999.[4] Since then, a scope of nickel NHC complexes capable of catalyzing the Suzuki—Miyaura cross-coupling was significantly extended.[5,7,31,51—55]

Dicationic Ni complex **1** described by Chiu *et al*.[8] showed "universal" catalytic activity and was found to catalyzed Suzuki cross-coupling involving aryl chlorides, aryl bromides, and aryl iodides.



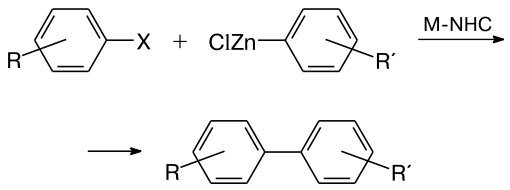
1

It was also shown that the Suzuki—Miyaura cross-couplings could be realized using palladium complexes of organoselenium chelators[56] and palladium nanoparticles as catalysts.[57] Namely, the Suzuki reactions could be conducted under phosphine-free and carbene-free conditions.

Negishi coupling is another widely used carbon—carbon bond forming reaction. The reaction couples organozinc reagents (more seldom organoaluminum and organozirconium reagents) with aromatic halides bearing different

functional groups (Scheme 8). Unfortunately, the data on the catalysis with NHC complexes of nickel and palladium in the Negishi coupling are scarce. Thus, until 2005 only two publications[58,59] related to application of palladium NHC complexes in the Negishi cross-coupling have appeared. On the other hand, the past decade has seen fast growing interest in catalysis of the Negishi coupling with the NHC complexes of nickel[11,15] and palladium.[60,61]

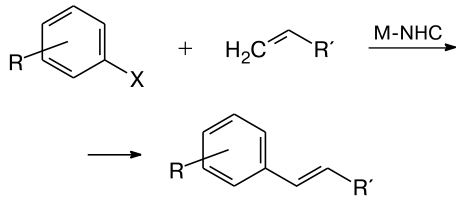
Scheme 8



X = Br, Cl, I; M = Ni, Pd

Heck reaction. It was found that NHC complexes of nickel and palladium are capable of catalyzing the Heck reaction, cross-coupling of activated olefins with aryl halides (Scheme 9).

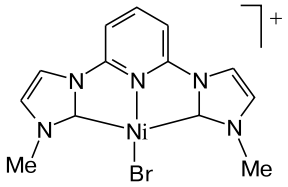
Scheme 9



X = Cl, Br, I; M = Ni, Pd

In the vast majority of publications describing the Heck reaction, the palladium complexes were used.[62—71] However, several examples of catalysis with nickel complexes are also reported.[31,72,73] It is notable that the nickel-catalyzed Heck reactions are less studied.

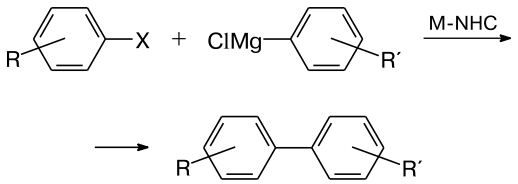
Nickel complex **2** showed excellent performance in the Heck reaction.[31] At low loadings of only 5 mol.%, this complex efficiently catalyzes the Heck reactions of aryl chlorides, aryl bromides, and aryl iodides in the presence of Na_2CO_3 and Bu_4NI as the bases.



2

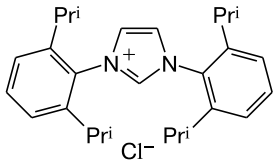
Kumada—Tamao—Corriu coupling reaction catalyzed by nickel and palladium complexes is of interest because it could be performed between the Grignard reagents and aryl halides; the reaction also tolerates some other substrates (Scheme 10). Despite the fact that the Grignard reagents suffer from moisture and air sensitivity, a large variety of organometal derivatives (organoboron, organozinc, organotin, organonickel species, *etc.*) were derived from the corresponding organomagnesium compounds.

Scheme 10



X = F, Cl, Br, I, OMe; M = Ni, Pd

Huang and Nolan[74] were the first to describe the Kumada—Corriu coupling mediated by palladium NHC complex in 1999. Catalyst was generated *in situ* from zerovalent palladium complex $[Pd_2(dba)_3]$ (dba is dibenzylideneacetone) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (**3**). This system efficiently catalyzes the Kumada cross-couplings. Soon, in 2000 and 2001, Herrmann and co-workers have demonstrated that nickel complexes (including nickel complex bearing ligand **3**) efficiently catalyze the Kumada reaction and the nickel NHC complexes have been found as active as palladium complexes.[75,76]



3

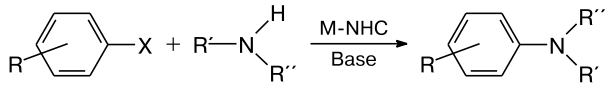
Later, the range of the catalytic systems catalyzing this process was extended and both palladium[77—79] and nickel[15,80—89] NHC complexes showed high catalytic performance.

Other cross-coupling reactions. Among other carbon—carbon bond forming reactions, cross-couplings of aryl bromides and aryl chlorides with organotitanium[89] and organomanganese[90] reagents in the presence of ligand **3** as the *N*-heterocyclic carbene source are notable. α-Arylation of ketones[91] and homocoupling of aromatic bromides (the Ullmann reaction)[92,93] catalyzed by nickel(II) NHC complexes were also described.

Some carbon—element (element is nitrogen, sulfur, *etc.*) bond forming reactions mediated by nickel NHC

complexes can also be regarded as the coupling reactions. The example of the carbon—nitrogen bond forming reactions is the Buchwald—Hartwig amination, the metal-NHC mediated cross-couplings of aryl halides with amines in the presence of strong bases (Scheme 11).

Scheme 11



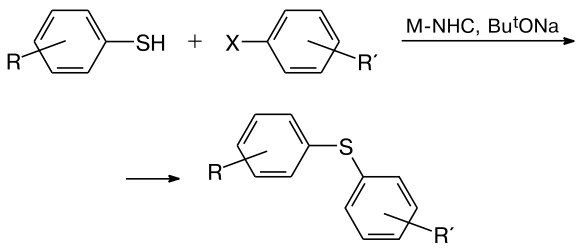
X = Cl, Br; M = Ni, Pd

This reaction is typically catalyzed by the palladium complexes including Pd-NHC complexes.[94] The Buchwald—Hartwig amination utilizes the primary and secondary amines, amides, NH-imines, and ammonia.[95] So far, this is the only cross-coupling reaction catalyzed by NHC complexes of palladium, catalytic cycle of which was extensively investigated by using both experimental and calculated data.[96—98]

Catalytic performance of the nickel NHC complexes in this reaction was well studied along with the palladium NHC complexes.[99—103] Thus, Fort and co-workers[104,105] described the cross-coupling of aromatic chlorides with different amines catalyzed by the *in situ* generated nickel(0) complex bearing 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium (SIPr) ligand. The nickel(0) species generated from $[Ni(acac)_2]$ (acac is acetylacetonate) by treatment with NaH and Bu^tOH associated with the SIPr ligand as the heterocyclic carbene source efficiently catalyze the cross-couplings of aromatic chlorides with cyclic and acyclic amines and the primary and secondary anilines providing good yields of the target products. Later, the scope of the nickel NHC complexes capable of catalyzing this transformation was extended.[36,106—112]

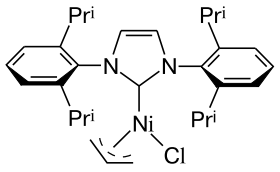
The sulfur—carbon bond forming reactions could be exemplified by the cross-coupling of aromatic thiols with aromatic halides (or alkynes)[113] (Scheme 12) giving rise to aromatic sulfides, the important precursors in pharmacology and biology.[114,115]

Scheme 12



X = Cl, Br; M = Ni, Pd

This reaction was efficiently promoted by (π-allyl)-nickel complex **4**.[116] Some other complexes capable of catalyzing this bond forming reaction are also known.[117,118]



4

Other examples of application of NHC complexes of palladium and nickel could be found in the reviews.[2,37,119,120]

Bellan *etc.*[121] published synthesis of cadmium(II) complex bearing bis-*O*-semiquinonato ligand. It is well known that complexes of redox-active semiquinones undergo reversible oxidation-reduction reactions in the coordination sphere of the metal.[122—124] In this case, the ligand serves as an "electronic storage" that allows varying the electronic structure of the metal complexes in a wide range.

Conclusions

To date, numerous carbon—carbon and carbon—element bond forming reactions catalyzed with the *N*-heterocyclic carbene complexes of nickel and palladium have been described. These reactions could be brought about by either preliminary synthesized stable sterically encumbered complexes or *in situ* generated catalysts. The last decade has seen the fast growing interest in the application of NHC metal complexes.

Along with palladium complexes conventionally used in cross-coupling reactions, NHC complexes of nickel emerge as active catalysts for those processes. At present, the actual issue of the large-scale industrial applications of the NHC-based catalysts is the reducing costs of their production and stabilization. The special attention is given to catalytically active compounds capable of withstanding a large number of catalytic cycles and to the nickel complexes, which can serve as the low-cost precursors to a catalytically active species. The increasing tendency of using the electrochemical methods for synthesizing these catalysts also should be noted.

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