===== REVIEW =====

Copper in Cross-Coupling Reactions: III.[1] Arylation of Azoles

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Abstract—The review discusses recently published data on copper-catalyzed arylation of azoles with aryl halides with the formation of new C–N bonds. Ligand-free catalytic systems, recyclable catalysts, and the use of water as solvent are considered.

Keywords: copper catalysis, cross-coupling, arylation of azoles, green chemistry, recyclable catalysts

1. INTRODUCTION

Nitrogen-containing heterocycles constitute structural units of many biologically active compounds, medicines [2], organic materials, ligands, and ionic liquids. Interest in the development of efficient and accessible methods for the synthesis of such compounds persists so far.
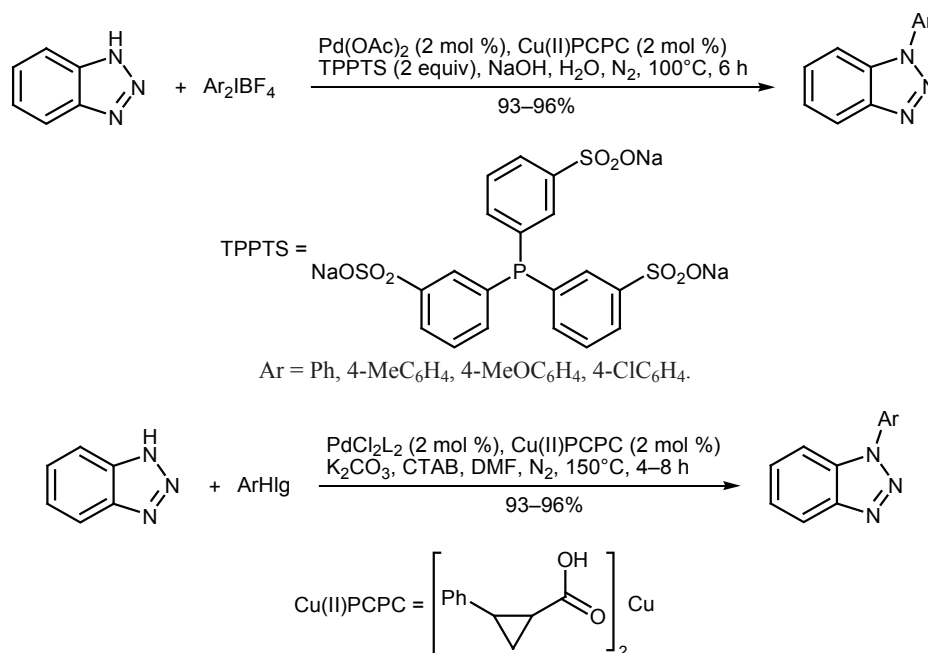
The formation of C–N bonds in reactions of amines with aryl halides [3] in the presence of copper compounds have been known long before palladium- and nickel-catalyzed protocols were developed. First examples of such reactions, in particular condensations of aromatic amines and amides with aryl halides promoted by copper compounds, have been reported by Ullmann in 1901–1903 and Goldberg in 1906. However, over a long time the Ullmann reaction required the use of copper in stoichiometric amounts, harsh conditions such as prolonged heating at a high temperature (150–200°C) [4], strong bases, and toxic solvents (nitrobenzene or pyridine) [5]. Therefore, the reaction scope was severely limited, and only electron-withdrawing aryl halides afforded high yields. Since the late 1990s, when metal-catalyzed methodologies utiliz-

ing mono- and N,N-, N,O-, and O,O-bidentate ligands were introduced, Ullmann arylation of nitrogen compounds under milder conditions has become possible [6–8]. For example, Buchwald and co-workers were among the first to perform successful arylation of imidazole with aryl iodides and bromides under catalysis by copper(I) salts in the presence of ligands [9].

Further development of a competitive, more efficient Pd-catalyzed C–N cross-coupling with the use of phosphine ligands according to the procedures proposed independently by Hartwig [10] and Buchwald [11] has marked a real breakthrough in the field of arylation of aliphatic and aromatic amines. However, the arylation of NH heterocycles under palladium catalysis proved to be somewhat limited for several reasons [12]. In particular, deprotonation of indole and pyrrole gives rise to ambident anions, so that Pd-catalyzed arylation of these substrates is not selective, and the yield is low, due to competitive formation of N- and $C^2(C^3)$-arylation products. This leads to the necessity of introducing substituents into the heterocyclic substrate molecule, empirical selection of phosphine ligands, or using stronger bases. Similar selectivity problems were encountered in the N-arylation of diazoles. It has become possible only with the use of bulky phosphine ligands such as XPhos, *t*-BuXPhos,
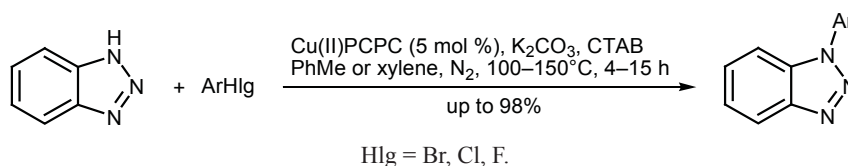
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[1] For communication II, see [1].

Scheme 1.

Pd(OAc)$_2$ (2 mol %), Cu(II)PCPC (2 mol %)
TPPTS (2 equiv), NaOH, H$_2$O, N$_2$, 100°C, 6 h

93–96%

TPPTS =

Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$.

PdCl$_2$L$_2$ (2 mol %), Cu(II)PCPC (2 mol %)
K$_2$CO$_3$, CTAB, DMF, N$_2$, 150°C, 4–8 h

93–96%

Cu(II)PCPC =

Hlg = I, Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-FC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-IC$_6$H$_4$, 4-CNC$_6$H$_4$, 4-AcC$_6$H$_4$, 4-EtOC(O)C$_6$H$_4$, thiophen-2-yl; Hlg = Br, Ar = pyridin-2-yl, pyridin-3-yl, quinolin-3-yl; L = DPPM, DPPE, DPPP, DPPB, DPPF; CTAB is cetyl(trimethyl)ammonium bromide.

Scheme 2.

Cu(II)PCPC (5 mol %), K$_2$CO$_3$, CTAB
PhMe or xylene, N$_2$, 100–150°C, 4–15 h

up to 98%

Hlg = Br, Cl, F.

and Me$_4$-t-BuXPhos that are required for the reductive elimination of the cross-coupling products. Available data on the Pd-catalyzed N-arylation of triazoles and tetrazoles are few in number.

In particular, the palladium-catalyzed arylation of benzotriazole with a diaryliodonium salt gave a mixture of N^1- and N^2-substituted isomers. However, the reaction in the presence of a catalytic amount of copper(II) salt selectively afforded the corresponding N^1-isomer in a high yield [13] (Scheme 1). Analogous reactions with aryl iodides and aryl bromides required more severe conditions [14]. Later on, proper choice of phase-transfer catalyst, solvent, and base made it possible to perform selective copper-catalyzed N^1-arylation of benzotriazole with electron-withdrawing aryl bromides, chlorides, and fluorides [15] (Scheme 2).

Palladium catalysts preferentially enable arylation of aliphatic and aromatic amino groups, whereas copper catalysts prove to be active toward a wider series of substrates, including amides, NH heterocycles, and cyclic aliphatic amines. This difference in the chemoselectivity of catalysts can be utilized for selective modification of molecules possessing several functional groups [16].

Thus, unlike catalysis by palladium complexes, copper-catalyzed N-arylation of NH heterocycles provides a convenient and available method for selective C–N bond formation, which does not require empirical selection and synthesis of complex phosphine ligands and (in many cases) inert atmosphere. Copper-catalyzed arylation of azoles can also be performed in water which is an environmentally safe, nontoxic, and inexpensive solvent.

2. ARYLATION OF AZOLES IN AQUEOUS MEDIUM

N-Arylation of NH heterocycles can be performed under considerably milder conditions in the presence of N,N-bidentate ligands (Fig. 1). Moreover, the use of
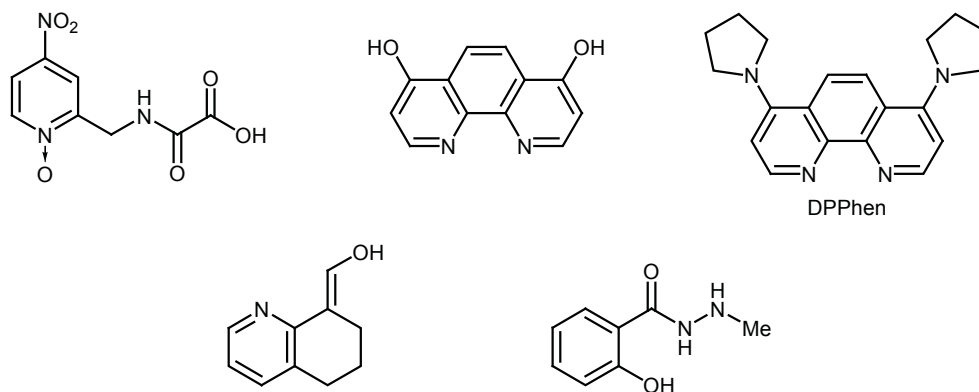
Fig. 1. Water-soluble ligands used in copper-catalyzed reactions.

ligands in combination with copper(I) and copper(II) salts and oxides, as well as with copper metal powder, provides arylation of NH heterocycles with aryl halides in water in the presence of a phase-transfer agent (R_4NX) [17–21] or other micelle-forming compounds such as choline chloride [22] or TPGS-750-M (water-soluble derivative of natural vitamin E) [23] and PEG [25], which significantly improve the solubility of the reactants.

In particular, copper(I) bromide (5 mol %) in combination with 4,7-di(pyrrolidin-1-yl)-1,10-phenanthroline (10 mol %) efficiently catalyzed arylation of imidazole and indole with aryl iodides and bromides [25].

The reactions were carried out in water containing PEG400 (20 mol %) at 100°C for 21 h (Scheme 3). Other nitrogen heterocycles also reacted with aryl halides in good to high yields under similar conditions. Unlike aryl iodides, the arylation of NH heterocycles with bromobenzene required a higher temperature (120°C) and longer reaction time (48 h). It should be noted that the given conditions enabled selective arylation of substrates containing an acetamide group or unprotected aliphatic amino groups, namely melatonin, 5-methoxytryptamine, histamine, 2-aminobenzimidazole, and purine bases (adenine and 2,6-diaminopurine). In some cases, the arylation of NH hetero-
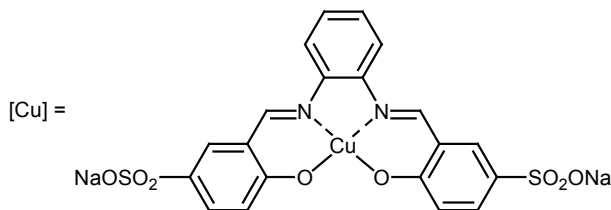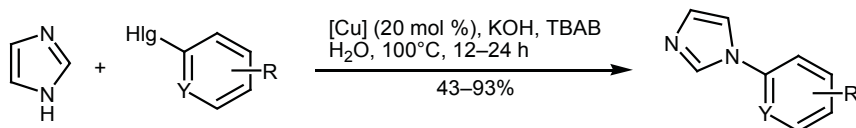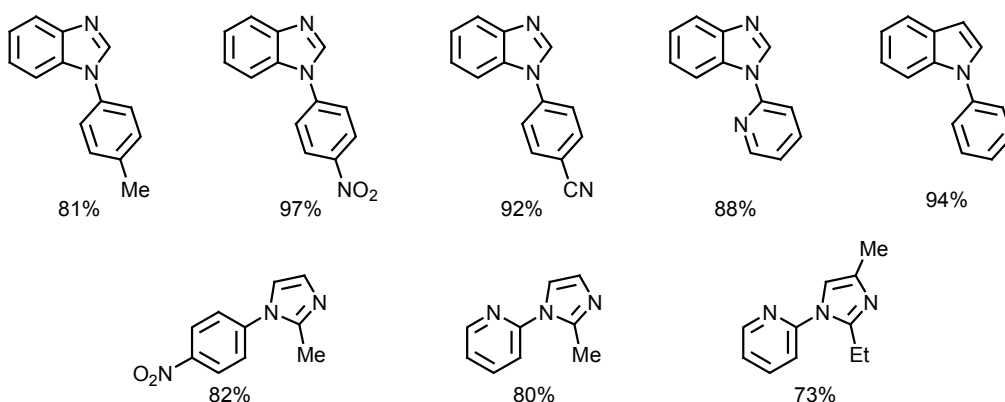
Scheme 3.
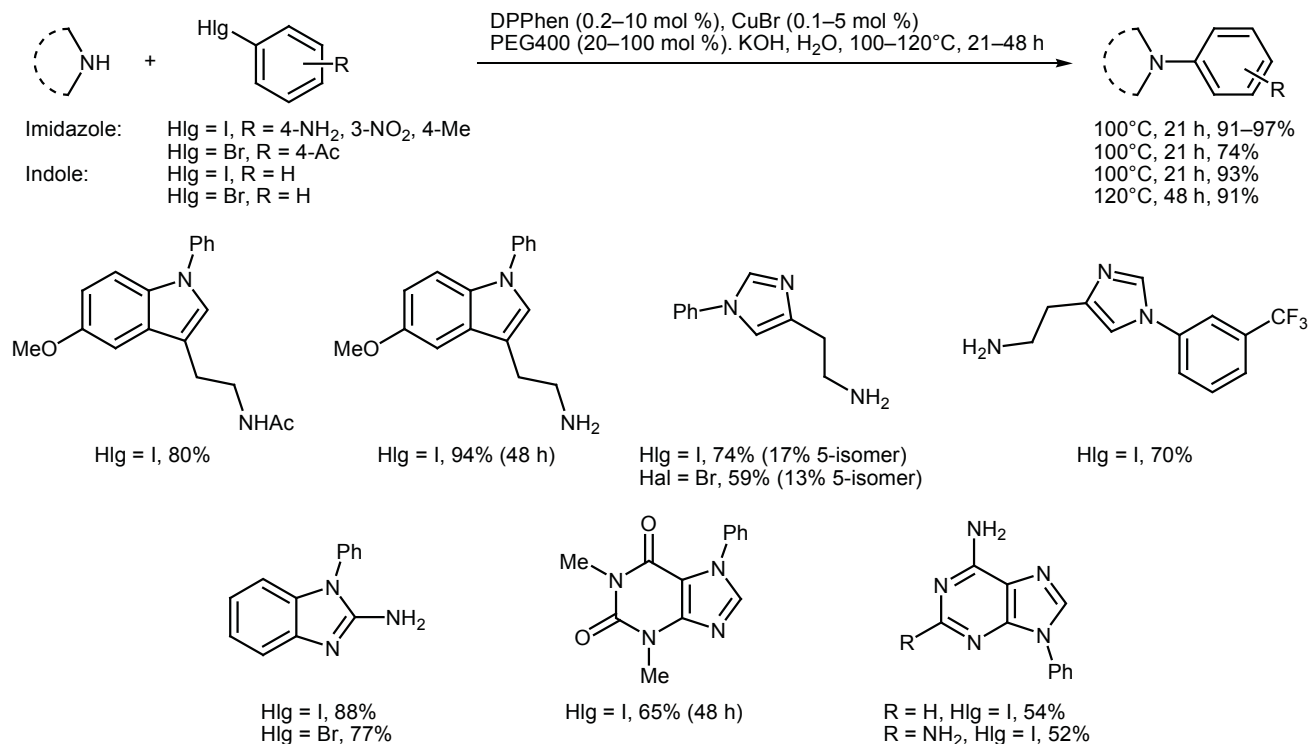
Scheme 4.
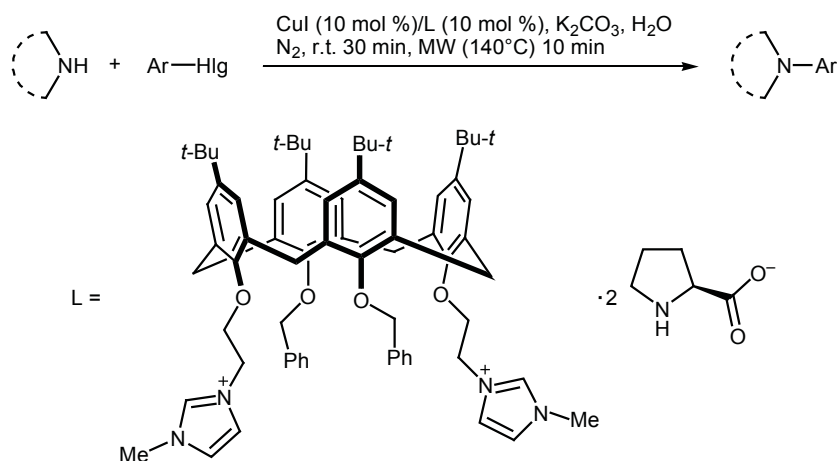
Hlg = I, R = 4-MeC$_6$H$_4$ (96%); Hlg = Br, R = Ph, 4-MeC$_6$H$_4$, 4-HC(O)C$_6$H$_4$, 4-H$_2$NC$_6$H$_4$, 4-EtOC(O)C$_6$H$_4$, naphthalen-1-yl, thiophen-2-yl (73–97%); Hlg = Cl; R = 4-O$_2$NC$_6$H$_4$ (98%).

Scheme 5.

Y = CH, Hlg = I, R = H, 4-Br, 4-Me, 4-NO$_2$; Hlg = Br, R = H, 4-MeO, 4-Me, 4-NH$_2$, 4-OH, 4-CN, 4-NO$_2$, 4-Ac, 4-CF$_3$; Y = N, Hlg = Br, R = H.

81%   97%   92%   88%   94%

82%   80%   73%

cycles can be performed in the presence of ligands and a stronger base even in the absence of phase-transfer catalyst [26–28].

The use of recyclable ligands [28, 29] and catalysts [30] contributes to the reduction of environmental pollution by industrial wastewater and production costs

and solves the problem of product purification from metals and ligands in scaled-up syntheses.

Microwave irradiation shortens the reaction time in the arylation of NH heterocycles in water from several days or hours to a few minutes [31, 32]. Su and co-workers [29] synthesized a ligand based on the calix-

[4]arene scaffold modified with ionic liquid fragments ([Emim][Pro]) and L-proline. This ligand in combination with copper(I) iodide (10 mol %, 1:1) catalyzed cross-coupling of NH heterocycles with various aryl halides in water under MW irradiation (Scheme 4). In this system, imidazole reacted with electron-donating and electron-withdrawing aryl bromides and 1-chloro-4-nitrobenzenes in up to 98% yield. The proposed catalytic system successfully worked in the arylation of benzotriazole, 1,2,4-triazole, pyrazole, and substituted indoles (yield 73–97%). The ligand was recycled in the reaction of 4-bromotoluene with imidazole by extraction of the product into ethyl acetate and reused at least three times (yields 93, 91, and 90% in the first, second, and third cycle, respectively). The authors presumed that the activity of the catalytic system is related to the ability of the ligand to act as phase-transfer agent.

Water-soluble salen copper(II) complex (2 mol %) promoted cross-coupling of azoles with aryl halides in water at 100°C [30] (Scheme 5). The presence of tetrabutylammonium bromide (TBAB) as phase-transfer catalyst was necessary to achieve high yields. Under these conditions, imidazole reacted with electron-deficient and electron-rich aryl iodides, as well as with aryl and hetaryl bromides, to afford 41–93% of the corresponding N-arylation products. Likewise, reactions of substituted imidazoles and indoles with aryl and hetaryl halides (Hlg = I, Br) furnished 73–97% of cross-coupling products in 12–24 h. The reaction of imidazole with 1-bromo-4-(trifluoromethyl)benzene (yield 88%, 12 h) was used as a model to investigate recyclability of the catalyst. After completion of the reaction, the product was extracted with ethyl acetate, new portions of the reactants, base, and phase-transfer catalyst were added, and the aqueous solution was

reused three times with yields of 87 and 84% in the first and third cycles, respectively.

Copper-catalyzed arylation of nitrogen heterocycles in water can also be performed without auxiliary ligands. High yields of N-arylation products were obtained in water using a phase-transfer catalyst and a base (LiOH, NaOH, K_3PO_4) under ligand-free conditions [33–35]. Successful N-arylation of NH heterocycles with aryl halides in the absence of ligands with high yields is also possible in organic medium. Some examples of such catalytic systems are considered below.

## 3. LIGAND-FREE COPPER-CATALYZED ARYLATION OF AZOLES

As a rule, ligand-free cross-couplings of NH heterocycles with aryl halides have significant drawbacks. In particular, these reactions require the use of large amounts (up to stoichiometric) of catalysts [36–38]; the range of aryl halides is generally limited to aryl iodides [39–43] and electron-withdrawing aryl bromides or chlorides; the reactions are carried out at higher temperatures [44, 45] than in the presence of ligands. The role of ligand may be played by the NH nucleophilic substrate [46], solvent, or base [42], but in these cases the efficiency of binding to active metal sites is lower.

As shown in [47], excess imidazole was necessary to achieve a high yield in the reaction with 4-bromoanisole; if an equimolar amount of imidazole was used, the yield was as low as 40%. The reaction was carried out in DMF at 120°C (40 h) in the presence of a base in an inert atmosphere (Scheme 6). Under the optimized conditions, imidazole reacted with electron-withdrawing and electron-donating aryl bromides and electron-
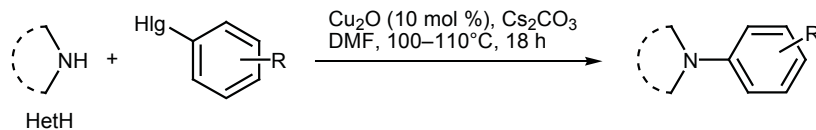
Scheme 6.

1.4 equiv
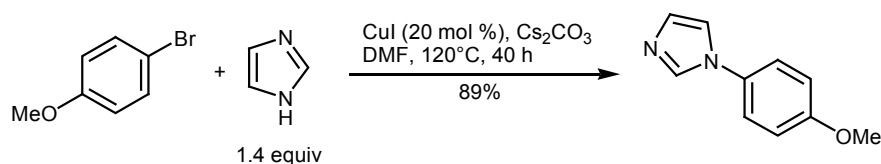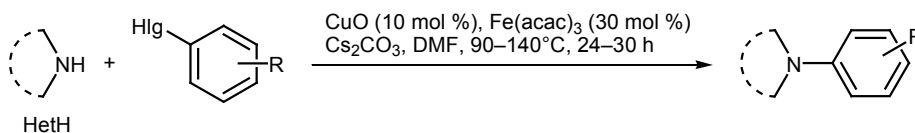
Scheme 7.

HetH = indole, imidazole, pyrrole, 1,2,3-triazole, 1,2,4-triazole, Hlg = I, R = H (up to 93%); HetH = pyrazole, Hlg = I, R = H, 4-COOEt, 4-OMe, 4-NH₂ (57–98%); Hlg = Br, R = H, 4-COOMe, 4-Me, 3-OMe, 4-OMe, 4-NO₂, 4-CN, 4-Ph (57–98%); Hlg = Cl, R = 4-CF₃ (40%).
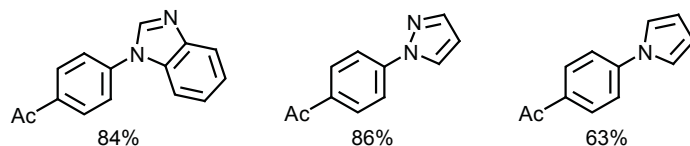
Scheme 8.

HetH = imidazole, benzimidazole, indole, pyrrole, 1,2,4-triazole, Hlg = I, R = H (up to 98%); HetH = pyraole, Hlg = I, R = H, 4-COOEt, 2-OMe, 2-Me (94–99%); Hlg = Br, R = H, 3-Me, 2-OMe, 3-NO$_2$ (91–99%); Hlg = Cl, R = 4-CN (98%).

Scheme 9.
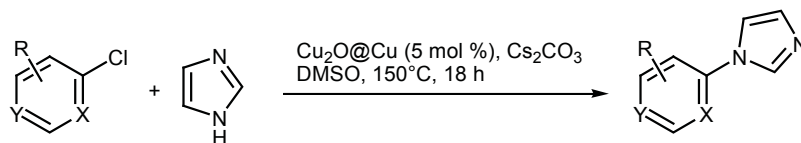
X = Y = CH, N, R = H (0%), 4-OMe (0%), 4-NO$_2$ (95%), 4-Ac (91%), 4-CF$_3$ (90%), 4-C(O)H (85%), 4-F (97%), 4-Cl (69%); X = CH, Y = N (86%); X = N, Y = CH (88%).

84%   86%   63%

withdrawing aryl chlorides to afford good to high yields, 56–98% (Hlg = Br) and 90–97% (Hlg = Cl). Reactions of iodobenzene with benzimidazole, substituted indoles, and 3,5-dimethylpyrazole (yield 63–95%), as well as of bromobenzene with 1,2,4-triazole (85%), pyrazole (84%), pyrrole (66%), and 2,2′-biimidazole (53%), were reported by the authors (the yields are given for the same reaction time). Substituted imidazole and pyrazole reacted with bromobenzene and iodobenzene, respectively, to give mixtures of regioisomers.

Both copper salts and its oxides effectively catalyzed arylation of azoles in the absence of additional ligands. Jiao et. al. [48] demonstrated a synergistic effect of copper and iron compounds in the catalysis of cross-coupling reactions. The bimetallic system CuO (10 mol %)/Fe(acac)$_3$ (30 mol %) in DMF at 90–120°C in the presence of a base catalyzed the reaction of pyrazole with electron-donating and electron-withdrawing aryl iodides (yield 91–98%) and aryl bromides (yield 81–98%) [49]. Pyrazole reacted with 4-iodoaniline and electron-donating aryl bromides at 120°C (24 h). However, only a moderate yield (40%) was achieved in the reaction of 1-chloro-4-(trifluoromethyl)-benzene even at a higher temperature (140°C, 24 h; Scheme 7). The bimetallic system was also efficient in the arylation of other azoles such as 1,2,4-triazole (83%), imidazole (90%), indole (93%), and pyrrole (91%) at 90°C (30 h). Under similar conditions, 1,2,3-triazole reacted with iodobenzene to produce a mixture of N^1- and N^2-arylation products in 48% and 41% yield, respectively.

Cheap and commercially available copper(I) oxide (10 mol %) catalyzed cross-coupling of pyrazole with electron-donating and electron-withdrawing aryl iodides and aryl and heteroaryl bromides in up to 99% yield (18 h) in the absence of ligands or other additives [50]. The reactions were carried out in DMF in the presence of a base in an inert atmosphere at 100°C for aryl iodides or 110°C for bromides (Scheme 8). These conditions made it possible to react pyrazole with 4-chlorobenzonitrile (yield 98%). Iodobenzene also reacted under the optimized conditions with the same reaction time with other azoles, namely 1,2,4-triazole (76%), benzimidazole (86%), indole (95%), and pyrrole (93%). The catalytic activity of Cu$_2$O (10 mol %) in the reactions of azoles with 2-, 3-, and 4-halopyridines was studied [51]. The model reaction of pyrazole with 3-iodopyridine was performed under ligand-free and solvent-free conditions under microwave irradiation using K$_3$PO$_4$ or Cs$_2$CO$_3$ as a base (yield 91%). The reactivity of halopyridines decreased in the series I > Br >> Cl ≈ ArF > OTf. The proposed system catalyzed cross-couplings of 3-iodopyridine with imidazole, pyrrole, and indole (yield 50–91%).

Copper(I) oxide immobilized on copper nanoparticles (Cu NPs), which were prepared by thermal decomposition of copper(II) acetylacetonate in the presence of oleylamine and subsequent oxidation with air, showed a high catalytic activity in reactions of

Scheme 10.
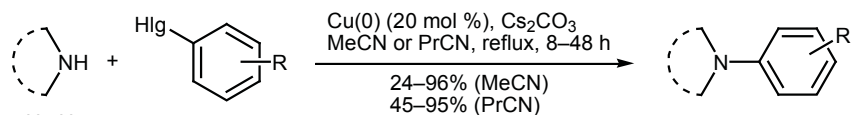
Hlg = I, R = H, 4-OMe, 4-NH$_2$, 2-Br, 4-NO$_2$, 4-COOEt; Hlg = Br, R = H, 4-OMe, 4-Cl.

Scheme 11.

HetH = indole, benzimidazole, imidazole, carbazole; Hlg = I, Br.
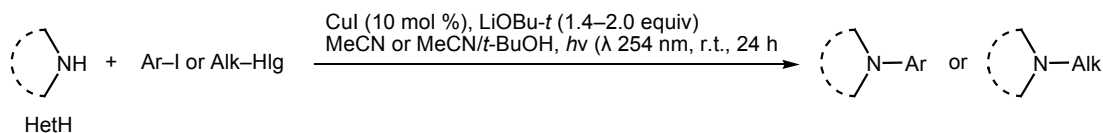
electron-withdrawing aryl chlorides with 2 equiv of benzimidazole, imidazole, pyrazole, and pyrrole in DMSO at elevated temperature (150°C) in the presence of a base [52] (Scheme 9). Chlorobenzene and 1-chloro-4-methoxybenzene failed to react with pyrazole under these conditions. Presumably, the activity of the catalyst prepared in this way is determined by not only large surface area of Cu NPs but also coordination of oleylamine as a ligand and copper on the surface of nanoparticles.

Hu et al. [53] reported an unusual autocatalytic effect in the cross-coupling of pyrazole with iodobenzene in acetonitrile in the presence of copper(0) powder (20 mol %). Presumably, the observed effect originates from the formation of active CuI species in the course of oxidative addition, which are stabilized due to coordination to the nitrile solvent as a ligand. Copper(0) powder in an amount of 20 mol % catalyzed the reaction of pyrrole with electron-withdrawing and electron-donating aryl iodides in acetonitrile (yield 85–96%) and butyronitrile (83–95%). Under similar conditions, aryl bromides reacted with pyrrole only in the presence of KI (for *in situ* halogen exchange) to afford 75–83% (MeCN) and 77–81% yields (PrCN). The same catalytic system was used to catalyze reactions of iodobenzene with pyrazole, imidazoles, indole, carbazoles, and ethyl 4-phenylpyrrole-3-carboxylate in up to 96% yield (Scheme 10). Only moderate yields were obtained in the reactions of 1,2,3- and 1,2,4-triazoles with iodobenzene even when the reaction time was prolonged to 48 h.

Scheme 11 illustrates ligand-free arylation of azoles at room temperature. A modified procedure for photoinduced CuI-catalyzed cross-coupling of iodobenzene and alkyl halides with carbazoles (λ 350 nm, 0–30°C) [54] was utilized for the first time in reactions of aryl halides with substituted NH heterocycles (λ 254 nm,

room temperature) [55]. The reactions were performed in acetonitrile or MeCN/*t*-BuOH in the presence of a base for 24 h. Aryl iodides reacted with benzimidazoles, imidazoles, carbazoles, and indoles with good to high yields (57–86%). Good yields were obtained in the reactions of bromobenzene with benzimidazole (62%) and indole (62%) and of 4-chlorobenzonitrile with carbazole (72%) and benzimidazole (61%). Apart from aryl halides, cross-couplings of alkenyl and alkynyl halides (Hlg = I, Br) with carbazole (Br: 63%, I: 75%, 85%) and indole (Br: 56%, I: 74%) were reported.

Unfortunately, the articles considered in this section contained no data on recyclability of the employed catalytic systems, though the development of recyclable catalysts is now of increasing interest in view of the possibility of significantly reducing production costs.

4. RECYCLABLE CATALYTIC SYSTEMS FOR ARYLATION OF AZOLES IN ORGANIC MEDIUM

Glycerol [56], ionic liquids [57, 58], poly(ethylene glycols) [59–62], and other solvents are also often used as recyclable reaction media for the arylation of azoles.

4.1. Heterogeneous Catalytic Systems

Of particular interest are heterogeneous catalytic systems due to the possibility of their multiple reuse. For example, insoluble copper salts and complexes with a multidentate pyridine [63] or phthalocyanine derivative [64] were successfully used as heterogeneous catalysts in the arylation of NH heterocycles and were recovered from the reaction mixtures for repeated use. Copper(II) phthalocyanine at a fairly low concen-

tration (1 mol %) catalyzed reactions of electron-donating and electron-withdrawing aryl iodides with indole, imidazoles, and pyrroles in up to quantitative yield. The reactions were carried out in DMSO at 100°C for 8–12 h in the presence of a base under aerobic conditions (Scheme 12). These conditions proved to be suitable for the arylation of indole with 4-bromoanisole (yield 94%) and of pyrrole with 1-chloro-4-nitrobenzene (73%). The catalyst was recycled five times in the cross-coupling of benzimidazole with 4-bromoanisole without loss of activity (yields 99 and 94% in the first and fifth cycles, respectively) [64].

Copper(II) oxide nanoparticles catalyzed cross-couplings of aromatic amines and amides and azoles with aryl iodides, bromides [65–67], chlorides [68], and even fluorides [69] both in an inert atmosphere and under aerobic conditions. In most cases, the catalyst was successfully recycled.

The reaction of imidazole with aryl halides (Hlg = I, Br, Cl) was catalyzed by Cu_2O in DMSO in the presence of a base [70] (Scheme 13). Imidazole also reacted with electron-withdrawing aryl and heteroaryl chlorides to give N-arylimidazoles in up to 89% yield.

The catalytic system worked well in the cross-couplings of iodobenzene with benzimidazole, pyrrole, pyrazole, and indole (yield 88–92%). Recyclability of the catalyst was studied in the reactions of iodobenzene with imidazole (yields 90 and 88% in the first and fourth cycles, respectively) and pyrrole (yields 91 and 89% in the first and fourth cycles, respectively).

Metal nanoparticles represent a promising and increasingly studied field of heterogeneous catalysis due to their high catalytic activity which is determined by their large surface area but small volume. The catalytic activity of nanoparticles can be tuned by variation of their characteristics such as size, morphology, and composition. Nanoparticles that are insoluble in organic solvents can be separated from the reaction medium. However, in some cases, nonstabilized nanoparticles may agglomerate to form inactive species, which restricts their repeated use and hampers regeneration.

Kantam et al. [71] revealed a unique catalytic activity and air stability of CuI NPs prepared by the hydrothermal method from $CuSO_4 \cdot 5H_2O$ and solutions of sodium citrate and potassium iodide. These nanoparticles, even at a low concentration (1.25 mol %),

Scheme 12.

X = CH, N; Hlg = I, R = H, 4-Me, 4-OMe, 4-NO$_2$ (95–100%); Hlg = Br, R = 4-OMe (94%);
Hlg = Cl, R = 4-NO$_2$ (73%).
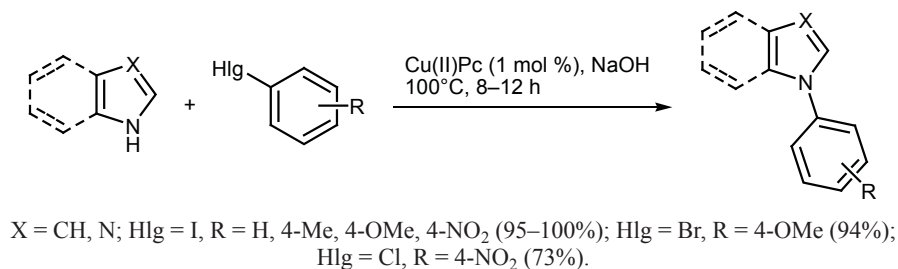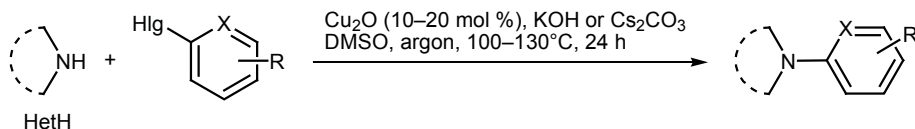
Scheme 13.

HetH = imidazole: Hlg = I, X = CH, R = 2,3-benzo, 2-Me, 3-Me, 4-Me, 4-OMe, 3-NH$_2$, 3-CF$_3$, 4-CN, 4-COOEt (85–92%); Hlg = Br:
X = N, R = H; X = CH, R = H, 4-CF$_3$, 4-NH$_2$, 4-Me, 3,5-Me$_2$ (88–91%); Hlg = Cl: X = N, R = H (88%); X = CH, R = 4-CF$_3$ (89%).
Hlg = I, R = H, HetH = pyrazole (92%), benzimidazole (88%), indole (90%), pyrrole (91%).

Scheme 14.
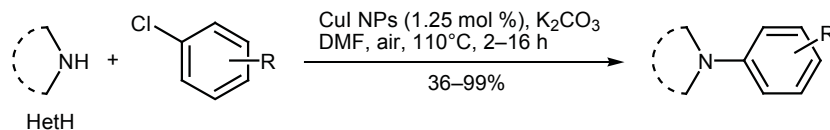
HetH = imidazole, benzimidazole, pyrazole; R = 4-I, 4-Cl, 4-Me, 4-OMe, 2-NO$_2$, 4-NO$_2$, 2-CN,
4-CN, 2-CHO, 4-CHO, 4-Br, 4-CF$_3$, 4-Ac.

Scheme 15.
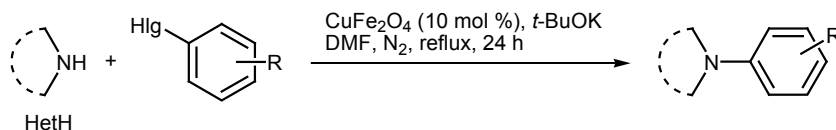
HetH = pyrrole, Hlg = I, R = H (72%), 4-COOH (99%); Hlg = Br, R = H, 4-NO$_2$, 4-Ac, 4-COOEt, 4-NH$_2$, 4-OMe (58–98%); Hlg = Cl, R = H (48%), 4-COOEt (40%), 4-OMe (20%); Hlg = Br, R = H, HetH = pyrazole (97%), 3,4-dimethylpyrazole (50%), imidazole (83%), 2-methylimidazole (59%), benzimidazole (85%), indole (90%), benzotriazole (75%), carbazole (82%).

catalyzed reactions of azoles with various aryl chlorides in DMF at 110°C in the presence of a base under aerobic conditions (Scheme 14). Imidazole, benzimidazole, pyrrole, and pyrazole reacted with aryl chlorides under the proposed conditions to afford cross-coupling products in up to 99% yield (2–16 h). The catalyst was recycled in the reactions of imidazole with 4-chloroanisole and 1-chloro-2-nitrobenzene, and the yields were 95 and 94% or 99 and 97% in the first and fifth cycles, respectively. After removal of the catalyst from the reaction mixture, no further coupling was observed in the absence of the catalyst.

The catalytic activity of CuFe$_2$O$_4$ NPs (10 mol %) was studied in reactions of azoles with aryl halides (Hlg = I, Br, Cl) in an inert atmosphere at a fairly high temperature (155°C) [71] (Scheme 15). The reactivity of aryl halides toward pyrrole as substrate decreased in the series ArI > ArBr > ArCl. Interestingly, pyrrole reacted with electron-rich aryl bromides in higher yields than with electron-deficient ones, the reaction time being the same. The nanocatalyst can be quantitatively separated from the reaction mixture using a magnet. It was recycled in the reaction of bromobenzene with pyrrole, and the yields were 98% in the first cycle and 96% in the third cycle. An insignificant leaching of catalytically inactive copper was also noted.

There are numerous reported examples of recyclable systems based on copper(0) and copper(I) and copper(II) salts and oxides immobilized on various inorganic and organic porous supports. Supported catalysts are of tremendous interest from the viewpoint of development of continuous flow technologies.

4.2. Supported Copper Complexes, Salts, and Oxides

Alper et al. [73] synthesized a hybrid material via immobilization of proline on the surface of a magnetite nanocomposite. Its combination with CuI (10 mol %) catalyzed the arylation of imidazole, pyrazole, indole, and benzimidazole with electron-withdrawing and electron-donating aryl and heteroaryl bromides in DMF at 110°C (24 h) in an inert atmosphere in the presence of a base (Scheme 16). After completion of the reaction, the magnetic material can readily be separated from the reaction mixture by using a magnet. The authors studied the possibility of ligand recycling in the reaction of 4-bromoacetophenone with imidazole. Provided that an additional amount of CuI was introduced, the ligand was recycled four times with an insignificant yield loss from 98% in the first cycle to 93% in the fourth cycle.

Subsequently, catalytic systems based on heterogenized copper(I) and copper(II) salts [generally CuI or Cu(OAc)$_2$] immobilized on various supports, including Fe$_3$O$_4$, have been proposed for the arylation of NH heterocycles [74–76]. Of great interest are other supports, in particular those based on modified silica [77–80] or aluminosilicates [81], polystyrene [82–85],

Scheme 16.
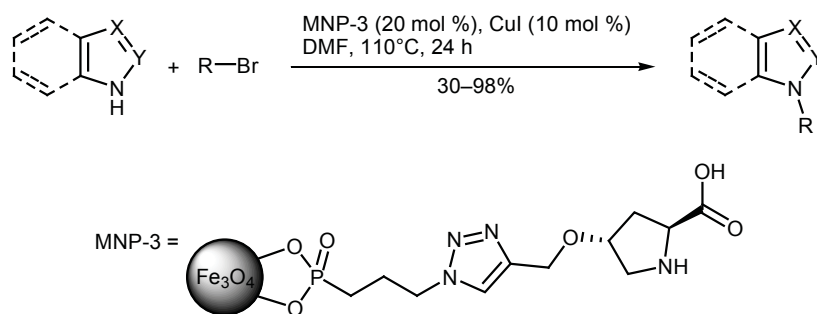
X, Y = CH, N; R = 4-AcC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-NCC$_6$H$_4$, 4-O$_2$NC$_6$H$_4$, pyridin-2-yl, thiophen-2-yl.

Scheme 17.
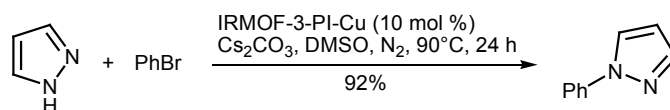
Scheme 18.

Hlg = I, R = H, 4-Me, 4-OMe, 4-NO$_2$, naphthalen-2-yl (3–14 h, 90–95%); Hlg = Br, R = H, 4-Me, 2-OMe, 4-NO$_2$, 4-C(O)H, pyridin-4-yl, pyrimidin-2-yl (2–15 h, 85–98%); Hlg = Cl, R = H, 4-NO$_2$, 2-NO$_2$, 4-CN, 4-Cl, pyridin-2-yl, pyrimidin-2-yl, 4-Me, 4-OMe, 2-CN-4-CF$_3$ (1–36 h, 52–95%; Hlg = F, R = 2-CN, 4-C(O)H, 4-NO$_2$, 2-Cl-4-NO$_2$ (0.5–1 h, 80–85%).
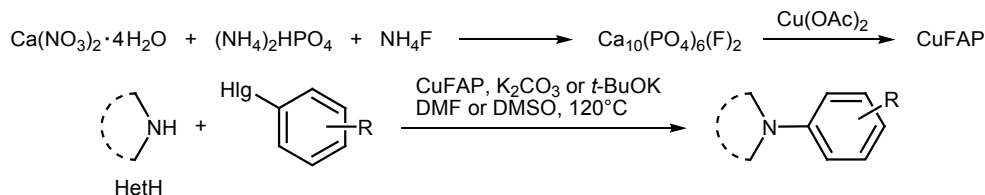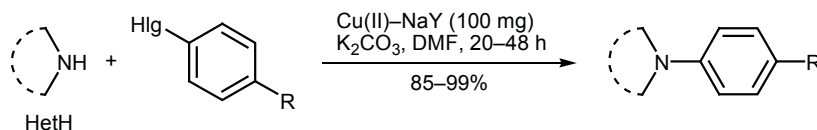
Scheme 19.

HetH = imidazole, benzimidazole, pyrazole, pyrrole, indole; Hlg = Cl, R = NO$_2$, CN, CF$_3$, Ac;
Hlg = Br, R = H, Ac, Me, OMe; Hlg = I, R = H, Me, OMe, Cl.

polyaniline [86, 87], resins [88, 89], and carbon nano-tubes [90]. The support surface is often modified with various N,N-, N,O-, or O,O-chelating ligands to stabilize copper salts immobilized thereon and prevent active species from being leached into solution.

Metal–organic frameworks (MOFs) constitute a separate promising group of heterogeneous catalysts. The key features of these materials are their stability and high porosity which enable fast mass transfer and interaction with substrates. The high catalytic potential of MOFs is determined by wide possibilities of tuning and controlling the cage structure and hence its properties. Metal–organic framework based on Zn(NO$_3$)$_2$ · 4H$_2$O and 2-aminoterephthalic acid (IRMOF-3) was modified with pyridine-2-carbaldehyde (PI) and Cu(II) (IRMOF-3-PI-Cu, copper content 4.7×10^{-2} mol %). As a result of this modification, the original hydrophilic and moisture-unstable IRMOF-3 became hydrophobic [91]. The obtained catalyst showed a high activity in the arylation of pyrazoles (including 3-substituted derivatives), imidazole, 1,2,4-triazole, and even 1,2,3-triazole in DMSO at 90°C (yield 70–99%, Scheme 17). 5-Methyl- and 2,5-dimethylpyrazoles, indazole, and benzimidazole turned out to be less reactive substrates toward aryl bromides (yield 28–73%), presumably for steric reasons. Aryl chlorides reacted with azoles in poor yields. The catalyst was recycled

five times in the reactions of bromobenzene with pyrazole (yield 92% in the first cycle and 90% in the fifth cycle), imidazole (90 and 87%), 1,2,3-triazole (83 and 82%), and 1,2,4-triazole (90 and 88%). No copper leaching into solution was observed in these reactions.

Heterogeneous copper-exchanged fluorapatite made it possible to perform arylation of NH heterocycles with not only aryl iodides and bromides [92] but also electron-rich aryl chlorides and electron-deficient aryl fluorides [93] (Scheme 18). Interestingly, some fluoro-arenes proved to be more reactive than their chlorine-containing analogs, and the reaction of 2-chloro-1-fluoro-4-nitrobenzene with imidazole selectively involved substitution of the fluorine atom. The catalyst was recycled four times without significant loss of activity. In the reaction of imidazole with bromobenzene, the yield changed from 90% in the first cycle to 89% in the fourth cycle, and in the reaction with 4-chlorobenzonitrile, from 100 to 90%. Deactivation of the catalyst was presumed to be caused by leaching of copper into solution where it was catalytically inactive.

The same research team developed a catalytic system based on Cu(II)-modified alkali exchanged zeolite Y [Cu(II)–NaY] for the arylation of imidazole with aryl halides (Hlg = I, Br, Cl) in 85–99% yield for

20–48 h. Other azoles such as pyrazole, indole, and pyrrole quantitatively reacted with 4-iodotoluene and 4-bromotoluene under the same conditions but did not react with 4-chlorotoluene [94] (Scheme 19). The catalyst was recycled four times in the reaction of imidazole with 4-bromotoluene, and copper leaching was 1.8% after the first cycle and 6.2% after the fourth cycle; the leached copper proved to be catalytically inactive.

Natural compounds were also used as supports and stabilizing ligands. For example, copper(II) oxide nanoparticles (CuO NPs) were prepared by mixing solutions of a copper(II) salt and aqueous leaf extracts of *Ocimum Sanctum* [95] and *Thymbra spicata* [96]. Presumably, the obtained CuO NPs are stabilized due to copper coordination to polyphenolic compounds present in leaf extracts. The biogenic CuO NPs prepared from *Ocimum Sanctum* leaf extract efficiently catalyzed the arylation of pyrrole, imidazole, benzimidazole, carbazole, and indole with various aryl iodides in DMF under aerobic conditions (80–91% in 12 h at 120°C). However, the catalyst was recycled only three times with an appreciable yield loss in the third cycle, which was rationalized by dissolution of the support during the reaction and subsequent aggregation and crystallization of CuO NPs. Copper(II) oxide NPs prepared from the *Thymbra spicata* leaf extract were active in reactions of indole and anilines with neutral and electron-donating aryl halides (Hlg = I, Br, Cl) in DMF at a fairly low temperature (40°C) under aerobic conditions (yield 65–98%, 1–12 h). The catalyst was recycled 7 times with insignificant loss of activity in the reaction of 4-chlorobenzene with aniline. The difference in the catalytic activities of copper(II) oxide nanoparticles is directly related to the procedures for their pre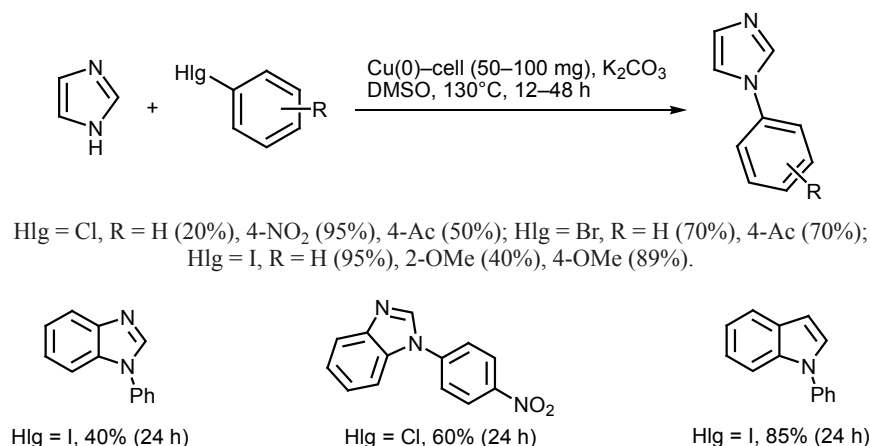paration, as well as with characteristics of the organic support/ligand which largely affect stabilization of copper(II) oxide.

Immobilization of finely dispersed highly active copper nanoparticles on various supports prevents their aggregation and favors their stabilization. Inert or weakly reactive highly porous materials with a large surface area are often used as supports. Nevertheless, the support often affects the properties of a metal immobilized thereon.
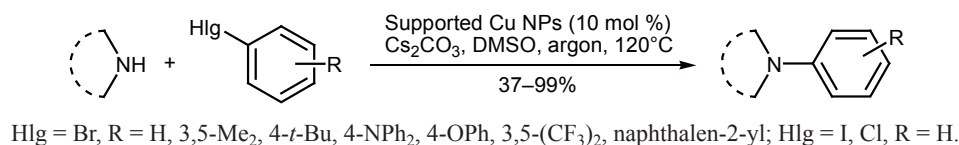
Microcrystalline cellulose-supported copper(0) catalyst showed a good activity in the reaction of imidazole with aryl halides (Hlg = I, Br, Cl) in DMSO at 130°C using triethylamine as a base [97]. Indole and benzimidazole also reacted with iodobenzene and 1-chloro-4-nitrobenzene under these conditions (Scheme 20). During the reaction, copper(0) is partially oxidized to copper(II) which is leached from the support in an amount of 0.8% after the first cycle to 3.5% after the fourth cycle in the reaction of imidazole with bromobenzene. Nevertheless, the catalyst was recycled four times in the reactions of imidazole with iodobenzene, 4-iodoanisole, and 1-chloro-4-nitrobenzene.

Nitrogen-rich copolymeric microsheets prepared by incomplete condensation of melamine and cyanuric chloride were used as a stabilizing support for finely dispersed Cu(0) nanoparticles with a size of ~10 nm [98], and the resulting material catalyzed N-arylation of pyrazole and imidazoles with aryl halides (Hlg = I, Br, Cl) in DMSO in the presence of Cs_2CO_3 as a base at 120°C in an inert atmosphere (yield 37–99%; Scheme 21). The catalyst was recycled four times in the reaction of bromobenzene with imidazole. However, the yield of the arylation product sharply dropped down to 50% in the fifth cycle, presumably due to
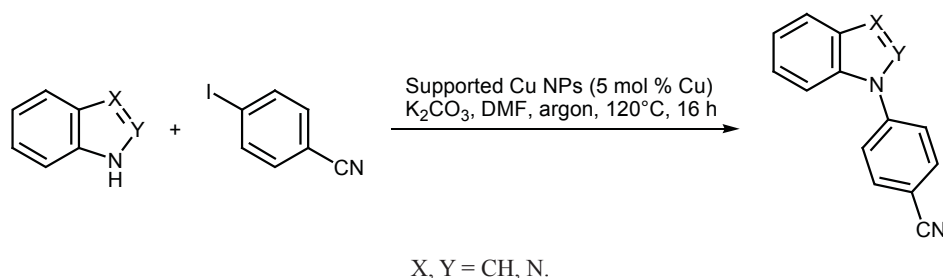
Scheme 20.

Hlg = Cl, R = H (20%), 4-NO₂ (95%), 4-Ac (50%); Hlg = Br, R = H (70%), 4-Ac (70%); Hlg = I, R = H (95%), 2-OMe (40%), 4-OMe (89%).

Hlg = I, 40% (24 h)   Hlg = Cl, 60% (24 h)   Hlg = I, 85% (24 h)

Scheme 21.

Hlg = Br, R = H, 3,5-Me$_2$, 4-t-Bu, 4-NPh$_2$, 4-OPh, 3,5-(CF$_3$)$_2$, naphthalen-2-yl; Hlg = I, Cl, R = H.

Scheme 22.

X, Y = CH, N.

Table 1. Arylation of azoles over supported Cu(0) nanoparticles

Azole	Yield, %			
	TiO$_2$	NaY zeolite	montmorillonite K10	charcoal
Imidazole	**90**	50	65	71
Pyrazole	**82**	**75**	**75**	**80**
Benzimidazole	**72**	49	68	61
Indole	**59**	36	41	59

change of the surface as a result of aggregation or passivation via capture of counterions (Br$^-$, CO$_3^{2-}$) from the reaction medium by nanoparticles. It is important that the main composition of the support did not change during the reaction, but active terminal hydroxy groups of the copolymer were transformed.

Copper(0) nanoparticles were immobilized on octadecylamine-modified montmorillonite [99], zeolites [100, 101], and various carbon supports (such as activated carbon [100], "acetylene black" [102], and graphene oxide [103]) and tested in the arylation of azoles. Presumably, the support could affect not only the catalytic activity and recyclability of nanoparticles but also the reactivity of azole substrates.

The catalytic activities of copper NPs immobilized on charcoal, montmorillonite K10, NaY zeolite, and nanosized titania were compared in the arylation of imidazole, benzimidazole, indole, and pyrazole with 4-iodobenzonitrile [100]. The reactions were carried out in DMF at 120°C for 16 h in an inert atmosphere using K$_2$CO$_3$ as a base (Scheme 22, Table 1). Titania-supported Cu NPs showed the highest catalytic activity and provided the highest yield in the reaction of imidazole with 4-iodobenzonitrile. Pyrazole was found to be the most reactive substrate in reactions catalyzed

by Cu NPs on different supports (yield 75–82%), whereas moderate to good yields (36–59%) were obtained using indole as substrate. Cesium carbonate as a base provided quantitative yields in the arylation of imidazole in the presence of all the tested catalysts. The yield of the cross-coupling product in the Cu NPs/TiO$_2$-catalyzed reaction of imidazole with 4-iodobenzonitrile decreased from 90% in the first cycle to 70% in the second cycle in the presence of K$_2$CO$_3$, and from 99 to 83% in the presence of Cs$_2$CO$_3$. This was rationalized by catalyst poisoning due to adsorption of the initial reactants on the support. Copper leaching from the support was insignificant, 0.02% after 4-h reaction (yield 44%). Analogous reduction of the yield from quantitative in the first cycle to 65 and 78% in the second cycle was observed in the model reaction catalyzed by zeolite- and montmorillonite-supported Cu NPs, respectively. However, activated carbon-supported Cu NPs were recycled three times in the model reaction without loss of activity (quantitative yield), but the yield in the fourth cycle sharply dropped to 61%, though with insignificant copper leaching into the filtrate (0.05%).

Copper(0) nanoparticles (3.0±0.8 nm) immobilized on maghemite modified with nanosized silica (MagSilica) efficiently catalyzed cross-coupling of

imidazole with various aryl iodides (yield 87–93%) and aryl and heteroaryl bromides (45–93%) in DMF at elevated temperature (152°C, 12–60 h) under aerobic conditions (Scheme 23). Imidazole failed to react with aryl chlorides under these conditions. Other azoles such as benzotriazole, pyrazole, indole, and pyrrole did not react with bromobenzene even for 24 h. After completion of the reaction, the catalyst can be quantitatively separated by using a magnet. The catalyst can be recycled three times without appreciable loss of activity in the reaction of bromobenzene with imidazole (yield 85 and 83% in the first and third cycle, respectively) [104].

Graphene-supported Cu NPs were prepared by the reduction of graphene oxide with L-ascorbic acid in the presence of copper(II) sulfate, followed by air oxidation of copper NPs surface to form a film consisting of Cu(I)/Cu(0) and Cu(II) at a ratio of 6:4 [103]. The obtained nanocomposite catalyzed arylation of imidazole with electron-deficient and electron-rich aryl iodides (up to 98% yield, 1 h), aryl bromides (up to 98%), and chlorobenzene (56%) in DMSO in the presence of a base (Scheme 24). Successful arylation of other azoles (benzotriazole, benzimidazole, substituted

indoles) in up to 94% yield was also achieved under these conditions. The catalyst can be recycled up to five times with appreciable decrease of the yield from 92% in the first cycle to 75% in the fifth cycle and copper leaching of 0.9% in the first cycle and 1.3% in the fifth cycle. The overall concentration of leached copper by the 5th cycle was 6.1%. This may be due to increase of the Cu(II) fraction in the film to a ratio of 7:3 with respect to Cu(I)/Cu(0) and adsorption of Br⁻ and CO_3^{2-} ions from the reaction solution.

Dabiri et al. [105] reported the arylation of imidazole with electron-withdrawing and electron-donating aryl iodides and bromides (yield 79–98%), as well as with chlorobenzene (yield 65%), catalyzed by copper nanoparticles incorporated on a mesoporous hexagonal carbon nitride (2.5 mol % Cu) [105]. The reactions were carried out in DMF in the presence of a base for 4 h (Scheme 25). The optimized catalytic system was also efficient in the arylation of substituted indoles, benzimidazole, 1,2,3- and 1,2,4-triazoles, and tetrazole with 1-bromo-4-nitrobenzene (yield 68–98%). The nanocomposite catalyst was successfully recycled in the reaction of imidazole with bromobenzene: the yield decreased from 91 to 77% by the eighth cycle.

Scheme 23.
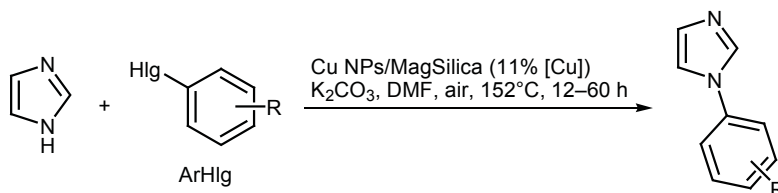
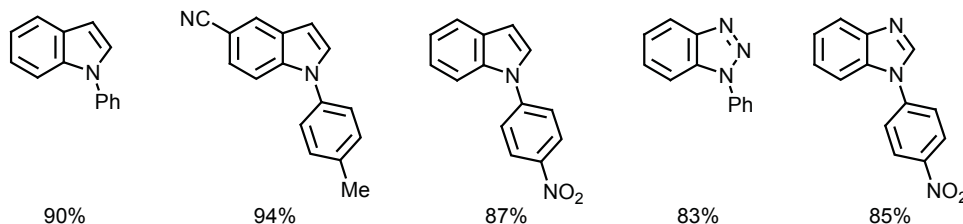Hlg = I, R = 4-Me, 4-Cl, 4-OMe, 2-NO₂ (12–18 h, 87–93%); Hlg = Br, Ar = naphthalen-1-yl, thiophen-2-yl, R = 4-Me, 4-Cl, 4-CHO, 4-OMe, 4-CH=CH₂, 4-Ph (21–60 h, 45–90%); Hlg = Cl, R = 4-Me (30 h, 10%).
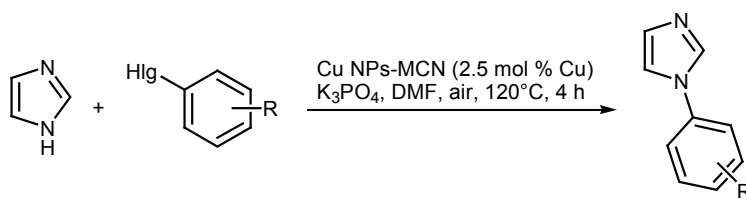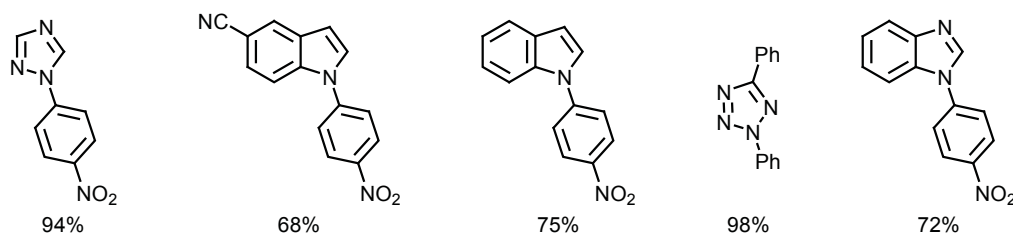
Scheme 24.
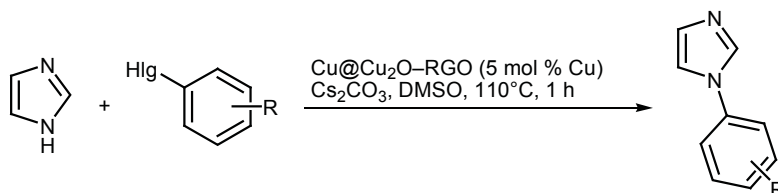
Hlg = I, R = H (96%), 4-NO₂ (98%), 2-Ac (98%), 4-Me (96%); Hlg = Br, R = H (92%), 4-Me (94%), 4-NO₂ (98%); Hlg = Cl, R = H (56%).

90%   94%   87%   83%   85%

Scheme 25.

Hlg = I, R = H (98%), 4-NO$_2$ (98%), 2-Me (86%), 4-Me (94%); Hlg = Br, R = H (91%), 4-Me (79%), 4-NO$_2$ (98%), 4-Ac (98%);
Hlg = Cl, R = H (65%).

94%   68%   75%   98%   72%

Scheme 26.

Z = Y = CH, X = N, Hlg = Cl, Br; Z = Y = N, X = CH, Hlg = Cl, R = H, 4-Me, 4-OH, 3-OMe, 4-OMe, 2-NO$_2$, 3-NO$_2$,
4-NO$_2$, 4-Ac, 2-CN, 4-CN, 3-cyanopyridin-2-yl, 6-chloropyridin-2-yl, 7-chloroquinolin-4-yl (55–99%); Hlg = Br, R = 4-Me,
4-OMe, 4-Cl (85–90%).

Mixed oxide Al$_2$O$_3$/SiO$_2$-supported copper nano-particles [Cu(0)@Al$_2$O$_3$/SiO$_2$] showed a high catalytic activity in the cross-coupling of azoles with various aryl chlorides in DMF under an inert atmosphere, but at a relatively high temperature (150°C) (Scheme 26). The yield decreased from 99% in the first cycle to 96% in the sixth cycle. Copper(0) nanoparticles were not oxidized on the support even by the fifth cycle, and no copper leaching was observed [106]. The catalytic activity of Cu(0)@Al$_2$O$_3$/SiO$_2$Na in the reaction of imidazole with 1-chloro-2-nitrobenzene (99% in 2 h) was compared with the activity of some other hetero-geneous catalysts [68, 80, 83, 91]. The proposed catalyst showed the highest TON and TOF values (19.8 and 9.9 h^{-1}, respectively) in the model reaction.

Thus, among the above considered catalytic systems for the arylation of azoles with aryl halides (including aryl bromides), the following deserve attention: copper iodide nanoparticles in combination with melamine–pyridine ligand [98] and CuFe$_2$O$_4$ [72]. Of particular interest are also those based on copper-exchanged fluorapatite [92, 93], copper iodide nanoparticles [71],

and Al$_2$O$_3$/SiO$_2$-supported Cu(0) nanoparticles [106], which showed a high activity in reactions of azoles with aryl chlorides.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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