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Metal-catalyzed reactions for the C(sp^2) – N bond formation: achievements of recent years

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The review deals with the main catalytic methods for the C(sp^2) – N bond formation, including Buchwald – Hartwig palladium-catalyzed amination of aryl and heteroaryl halides, renaissance of the Ullmann chemistry, *i.e.*, the application of catalysis by copper complexes to form the carbon – nitrogen bond, and Chan – Lam reactions of (hetero)arylboronic acids with amines. Also, oxidative amination with C – H activation, which has been booming during the last decade, is addressed. Particular attention is paid to achievements in the application of heterogenized catalysts.
The bibliography includes 350 references.

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1. Introduction

The discovery of cross-coupling reactions catalyzed by palladium(0) complexes in the 1970s was a highly important achievement that substantially changed the strategy of organic chemistry. Although the Nobel Prizes in Chemistry of 2010 were awarded for reactions concerning the C(sp^2) – C(sp^2) bond formation, no less important are other types of cross-coupling reactions giving carbon – carbon bonds, *e.g.*, involving carbon oxide (carbonylative cross-coupling), and carbon – heteroatom (N, O, S, Se, P) bonds. A special place among these processes is occupied by C(sp^2) – N bond formation reactions. It is well known that these bonds are present in numerous natural products, medicinal agents, agrochemicals and organic materials. Meanwhile, particularly the C – N bond formation *via* cross-coupling reactions proved to be the greatest challenge. The cause for this is obvious: the catalytic cycle of reactions of this type includes a transmetallation step involving participation of the anion of the reacting nucleophile. One more difficulty of amination, unlike the formation of the C(sp^2) – C(sp^2) bond, is the influence of the reductive amination step on the possibility for the reaction to occur. These fundamental problems have been successfully solved since the mid-1990s in the studies on the Pd-catalyzed amination.

Meanwhile, just several years after the first studies on the use of palladium complexes to form the C(sp^2) – N bond, alternative methods involving less expensive copper catalysts started to be developed. On the one hand, the same reactions of aryl iodides and aryl bromides with amines were used, and this was called the renaissance of Ullmann chemistry, but on the other hand, it was possible to use arylboronic acids instead of aryl halides. Subsequently, the catalytic oxidative amination with CH-activation started to be actively developed. In this case, the presence of a halogen or boron atom in the substrate is no longer necessary, but an important role is played by directing groups, which boost the C(sp^2) – H bond conversion to the C(sp^2) – N bond.

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These diverse methods for the nitrogen–carbon bond construction constitute the subject of this review.

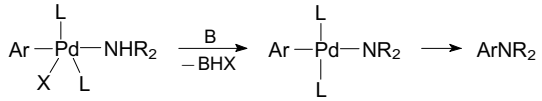
2. Palladium-catalyzed amination of (hetero)aryl halides

2.1. Early development of methodology of Pd-catalyzed C–N bond formation

Currently, there are hundreds of publications devoted to the development of methodology of carbon–nitrogen bond formation that consider various aspects of the palladium-catalyzed amination. Recently, several reviews on this subject were published.[1–4] Therefore, in this review, we address the most important aspects of this reaction, first of all, the influence of the ligand nature on the course of amination, with the attention being focused on the achievements of recent years.

In the case of free amine, the formation of an anion from a basic amine is problematic; this brings about the problem of decreasing the basicity of the nitrogen atom. A reaction of C(sp^2)–N bond formation was first described in 1983 by Migita and co-workers,[5] who used aryl bromides and tin amides and catalysis by palladium chloride $PdCl_2$ and P(*o*-Tol)$_3$ ligand [Tol is methylphenyl (tolyl)]. When palladium compounds are used as catalysts, the N–H bond in the intermediate complex is acidic and, hence, the base is capable of abstracting a proton to form the amide complex, which is converted to the product $ArNR_2$ upon reductive elimination (Scheme 1).

Scheme 1

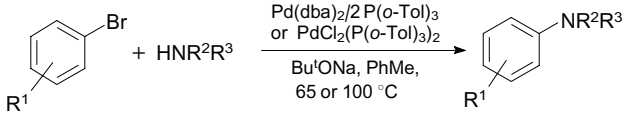


L is ligand, X is the leaving group (halogen atom),
R is alkyl or aryl substituent, B is base

Back in 1984, it was shown for a single example that in the presence of 1.5 equiv. of $Pd(PPh_3)_4$, reductive amination of aryl bromide may take place to give a β-carboline.[6] After preliminary study of the applicability of stannyl derivatives of amines for elucidating the mechanism and modifying the conditions of the Kosugi–Migita reaction,[7,8] in 1995, Buchwald and co-workers[9] and Louie and Hartwig[10] independently published papers in which they used amines themselves, but not their stannyl derivatives, for amination in the presence of a catalytic amount of the palladium complex with tri(*o*-tolyl)phosphine (Scheme 2).

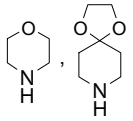
Scheme 2

Buchwald:

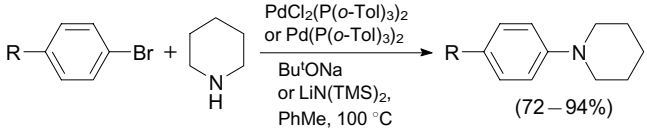


R^1 = 4-Ph, 4-Bz, 4-NMe_2, 3-OMe, 3-CF_3;

HNR^2R^3 = n-$HexNH_2$, PhNHMe, BnNHMe,



Hartwig:



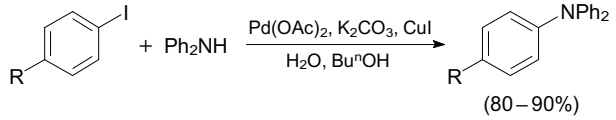
R = H, Bu^n, OMe, CF_3; dba is dibenzylideneacetone
Hex is hexyl, TMS is trimethylsilyl

Subsequently, both research groups succeeded in developing the amination methods for aromatic compounds with diverse amines: primary, secondary, cyclic, aliphatic and aromatic amines and ammonia. It soon turned out that the amination reactions often require the use of fairly specific ligands; however, this stimulated the synthesis of a variety of phosphine ligands with high efficiency. The success was impressive: owing to appropriate selection of the electron-donating and sterically hindered ligands, the amination of aryl chlorides can be carried out under mild conditions. This reaction was deservedly named the Buchwald–Hartwig reaction.

As compared with the cross-coupling reactions giving the C(sp^2)–C(sp^2) bond, which was the subject of the Nobel Prize in 2010, amination is a more complicated task. The implementation of the transmetallation step requires the formation of nucleophile in the anionic form, but the deprotonation of the basic amino group is fairly problematic. This is why the way from the reaction with tin or boron amide to reactions with free amines was so long.

However, it should be mentioned that at the end of 1995, Beletskaya and Davydov[11] accomplished the reaction of aryl halide with diphenylamine catalyzed by palladium in the presence of CuI without a ligand in aqueous butanol (Scheme 3). Note that the authors did not intend to create an amination method. They further developed the previously proposed approach to various types of cross-coupling in water or in aqueous media catalyzed by ligand-free palladium by attempting to extend it to reactions giving carbon–heteroatom bonds, particularly the C(sp^2)–N bond.

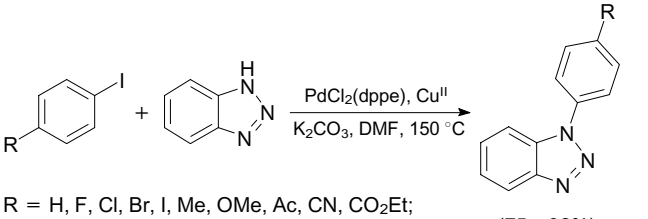
Scheme 3



R = H, Cl, Me, OMe

Subsequently, arylation of benzotriazole was carried out under similar conditions (Scheme 4).[12] However, it turned out that the palladium-catalyzed reaction gives a mixture of isomeric products of amination at positions 1 and 2; only the addition of a copper salt results in the selective formation of the arylation product at the N(1) atom.[12]

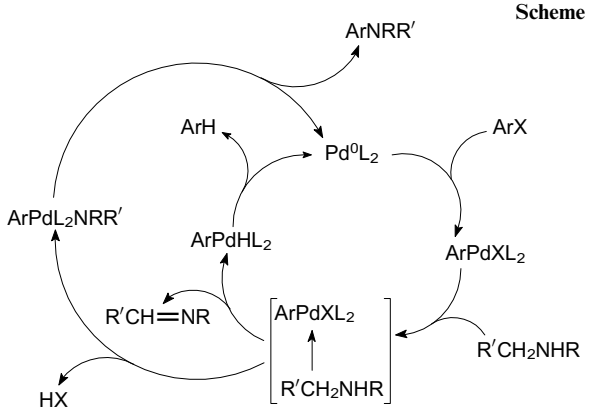
Scheme 4



R = H, F, Cl, Br, I, Me, OMe, Ac, CN, CO_2Et;
dppe is 1,2-bis(diphenylphosphino)ethane

Since this reaction is sensitive to the nature of the aryl halide and amine, careful choice of the ligand, the base and the solvent is required. First of all, we will consider the ligand issue. Even the first attempts of the Buchwald and Hartwig to use the Kosugi and Migita catalytic system for arylation of aliphatic amines demonstrated that this system is suitable for reactions of secondary amines in the presence of bases, but is inefficient in the reactions of primary amines. In this case, the competing hydrodehalogenation reaction, which always accompanies amination, becomes predominant. As a result, instead of complex ArPdNRR′, palladium hydride complex ArPdH is formed, which finally gives rise to ArH (Scheme 5).[3, 13]

Scheme 5



It is known that particularly the use of phosphine ligands made possible the first palladium-catalyzed cross-coupling giving $C(sp^2)-C(sp^2)$ bond. However, the choice of the ligand is especially important for the cross-coupling to form the $C(sp^2)-N$ bond. This issue is considered in numerous publications describing a variety of ligands, which allowed for conducting these reactions even for poorly reactive aryl chlorides. However, other factors such as the catalyst precursor, the solvent, the base and the temperature are also important, and certainly the nature of amine plays the crucial role. All these factors are interrelated and can affect one another.

2.2. Phosphine ligands in palladium-catalyzed amination

While starting their studies on the amination of aryl halides, Buchwald and Hartwig used bidentate ligands — 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and 1,1′-bis(diphenylphosphino)ferrocene (dppf), respectively — in the presence of a strong base (sodium *tert*-butoxide). Exactly the use of these systems enabled reactions with primary and secondary amines.[14, 15] Bidentate ligands such as BINAP, possessing a chelating effect, ensure the predominance of reductive elimination over the β-hydride elimination. They not only provide a higher reaction rate, but also make it possible to aminate the least reactive aryl tosylates and aryl chlorides under fairly mild conditions.[16] Subsequently, the range of aromatic bidentate ligands designed for these processes was supplemented by DPEPhos, XantPhos and NiXantPhos (Fig. 1).

These ligands were used to perform coupling of aryl chlorides not only with amines,[17] but also with various N-nucleophiles such as amides, sultams and ureas.[18 – 20] It was shown that the use of XantPhos enables the palladium-catalyzed arylation of aniline with aryl trifluorosulfonates.[21] The use of catalytic amounts of metal trifluoromethanesulfonates (triflates) (Al, Zn, In, Sc, Yb) accelerates coupling of aryl bromides with amides catalyzed by the $Pd(dba)_2$/XantPhos system *via* the exchange of the halogen atom with triflate,[22] while in the presence of NiXantPhos, coupling of secondary amines with aryl chlorides was successfully performed.[23] 2-(Dimethylamino)-2′-(dicyclohexylphosphino)biphenyl (DavePhos), a mixed P,N-bidentate ligand proposed by Buchwald,[24] exhibits a high activity towards amination of not only aryl bromides, but also aryl chlorides (Scheme 6).

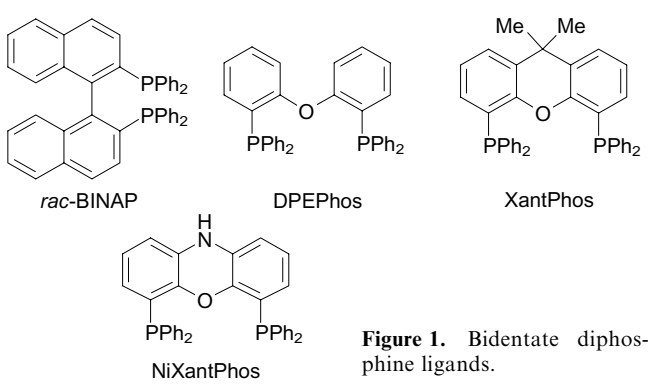
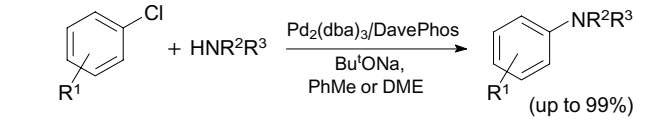
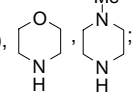


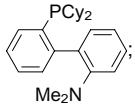
Figure 1. Bidentate diphosphine ligands.

Scheme 6



R^1 = 4-Me, 4-OMe, 2-OMe, 3-OMe, 4-CN, 3-CN, 4-NO_2, 2-NO_2, 4-Ac, 3-CO_2Me, 2-CO_2Me;

HNR^2R^3 = $BnNH_2$, Bu^nNH_2, PhNHMe, $XC_6H_4NH_2$ (X = H, 2-OMe, 4-OMe, 3-Me, 2-CO_2Et), ;

DavePhos = ; DME is dimethoxyethane, Cy is cyclohexyl

It was found that the electron-donor, first of all, sterically encumbered monophosphine ligands are also active in the amination reactions (Fig. 2).

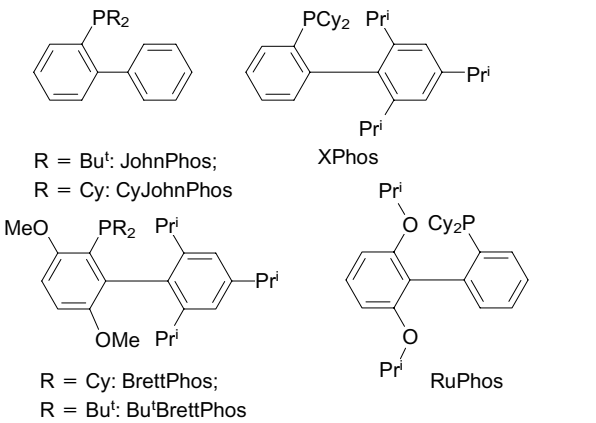
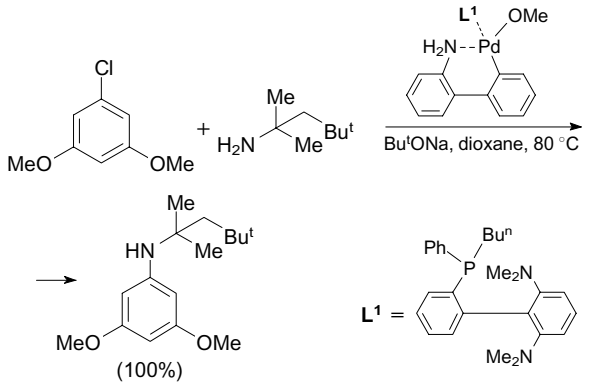


Figure 2. Ligands based on 2-phosphinobiphenyl.

In a review called 'a user's guide' and addressing the problem of choice of the ligand depending on the nature of amines and arylating reagents, Buchwald and co-workers [25] gave direct recommendations to synthetic chemists on how to choose the most appropriate ligand for the arylation of amines [primary, secondary, cyclic, acyclic, aliphatic and (hetero)aromatic amines], amides, ureas, carbamates and sulfamides, considering nine practically used biarylmonophosphine ligands as examples.

The amination of aryl chlorides with various amines was successfully implemented using the JohnPhos and CyJohnPhos monophosphine ligands.[24] The sterically more encumbered XPhos ligand enabled the amination and amidation of aryl sulfonates;[26] the same ligand proved to be efficient in the amination of (hetero)aryl chlorides [27] and also made it possible to accomplish the selective synthesis of di- and triarylamines from ammonia.[28] Further development involved the use of BrettPhos. This ligand was used to perform amination of aryl mesylates and selective monoarylation of primary amines with aryl chlorides,[29] while structurally similar Bu^{t}BrettPhos catalyzed the arylation of amides with aryl chlorides.[30] One more sterically encumbered ligand, RuPhos, was especially efficient in the reactions of secondary amines with aryl chlorides.[31] Among these ligands, mention should be made of the mixed P,N-ligand $\mathbf{L}^1$, which promotes the arylation of sterically hindered amines with aryl chlorides; in this case, palladium is present as a cyclopalladate (Scheme 7).[32]

Scheme 7

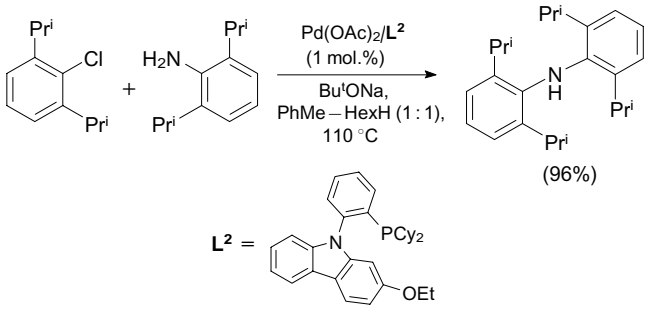


Recently, a palladium complex with substituted carbazole $\mathbf{L}^2$ was proposed as the catalyst for successful amination of sterically hindered aryl chlorides with also sterically hindered amines.[33] This catalyst proved to be so active that only minor concentrations of the catalyst (0.03 – 1 mol.%) were needed for the reaction (Scheme 8).

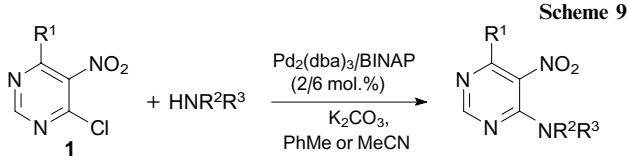
The activation of the chlorine atom in 5-nitropyrimidine derivatives **1** made it possible to obtain products in up to 96% yields by reactions with aliphatic and aromatic amines catalyzed by the Pd^0/BINAP system (Scheme 9).[34]

The effect of substituents in various positions of the aromatic or heteroaromatic ring on the aminodehalogenation reaction was considered for the reactions of 2-chloro- and 2-bromo-5-fluoropyridines with various amines in the presence of the Pd^0/XPhos catalyst (Scheme 10). The product yield depended on the nature of amine and varied over a very broad range, from 96% for butylamine to 25 and 15% for aniline and benzylamine, respectively.[35]

Scheme 8



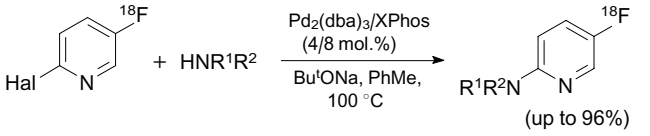
Scheme 9



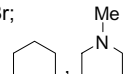
(81 – 99% ($R^1 \neq$ Cl); 10 – 80% (R^1 = Cl))

R^1 = Cl, NH_2, NHAlk, NHAr, $NAlk_2$, NAr_2;
HNR^2R^3 = $MeNH_2$, Pr^iNH_2, cyclo-$C_5H_9NH_2$, $XC_6H_4NH_2$ (X = H, 2-OMe, 3-OMe, 4-OMe, 2-CN, 3-CN, 4-CN), PhNHMe, morpholine

Scheme 10

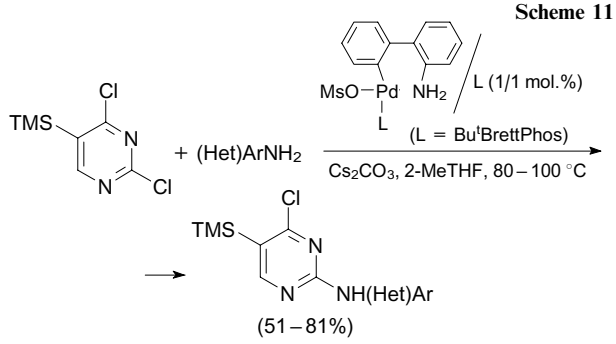


Hal = Cl, Br;

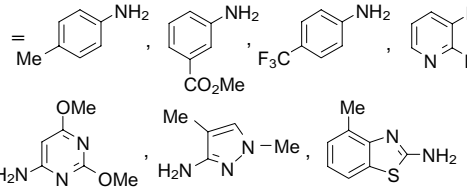
HNR^1R^2 =  , , Me_2NH, Bu^nNH_2, $BnNH_2$, $PhNH_2$, 3-$PyNH_2$; Py is pyridyl

The use of sterically hindered ligands to increase the selectivity of amination was studied in relation to the reaction of 2,4-dichloro-5-(trimethylsilyl)pyrimidine with aromatic and heteroaromatic amines catalyzed by cyclopalladate complexes with Bu^{t}BrettPhos (Scheme 11). The selectivity of replacement of the chlorine atom in position 2

Scheme 11



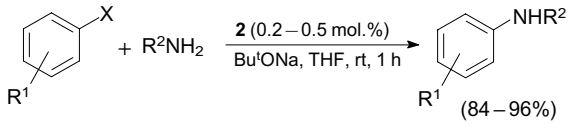
Ms = $MeSO_2$;

(Het)$ArNH_2$ = 

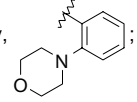
proved to be very high (99 : 1 for positions 2 and 4), irrespective of the nature of the amine, which is due to pronounced steric hindrance at the chlorine atom in position 4 in the case where the bulky phosphine ligand is used.[36]

One more sterically encumbered ligand, a polysubstituted biphenyl derivative, was used as a part of the catalyst, which demonstrated a broad range of applicability to amination reactions.[37] In the presence of a minor amount of catalyst **2** (mainly 0.2 – 0.5 mol.%), this reaction proceeded at room temperature for sterically hindered amines and electron-deficient anilines and also amines sensitive to bases. The target products were obtained in high yields within 1 h (Scheme 12).

Scheme 12

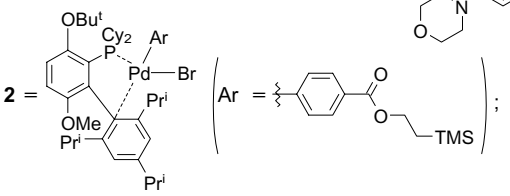


X = I, Br, Cl, OTf; R^1 = H, 2-OPr^i, 3-Me, 4-CO_2Me, 4-OMe, 4-SO_2Me;
R^2 = 2-$F_3CC_6H_4$, 2,6-$F_2C_6H_3$, 4-ClC_6H_4, 2,6-$Pr^i_2C_6H_3$,
$Bu^tCH_2CMe_2$, $HO(CH_2)_6$, CF_3CH_2, Cy, 2-Py,



;

2 =

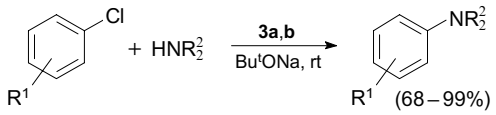


;

Tf is trifluoromethanesulfonyl (triflyl), rt is room temperature

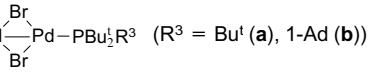
Sterically encumbered trialkylphosphines, *e.g.*, tri(*tert*-butyl)phosphine described earlier by Littke and Fu,[38] which provide the arylation of indoles and carbamates, were studied under Hartwig's supervision.[39] During further studies, it was proposed[40] to utilize the preliminarily prepared air-stable dimeric complexes **3a**,**b** with the composition PdBrL, where L = Bu^t_2P(1-Ad) (Ad is adamantyl) or Bu^t_3P, for reactions of secondary aliphatic amines with aryl chlorides, which proceeded at a high rate (Scheme 13).

Scheme 13



R^1 = 4-Me, 2-Me, 4-CN, 4-NO_2, 4-CO_2Bu^t;
R^2 = Bu^n; R^2 – R^2 = $(CH_2)_2O(CH_2)_2$;

3 =

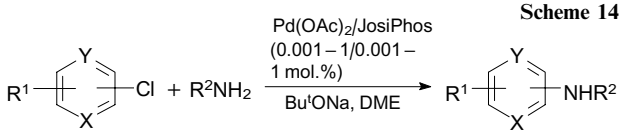


(R^3 = Bu^t (**a**), 1-Ad (**b**))

Subsequently, Hartwig[41] employed phosphine ferrocene derivatives of the JosiPhos family, which possessed appropriate steric and electronic properties (Scheme 14).

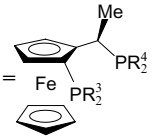
Using these ligands, the indicated reactions could be performed for problem heteroaryl halides capable of substituting ligands in palladium complexes or for amines prone to form diarylation products. High selectivity was attained at low palladium and ligand concentrations. The

Scheme 14



X, Y = CH, N; R^1 = Me, CN, C(O)NH_2, CO_2H;
R^2 = *n*-Oct, Bu^i, Bu^s, Bu^t, Bn (Oct is octyl);

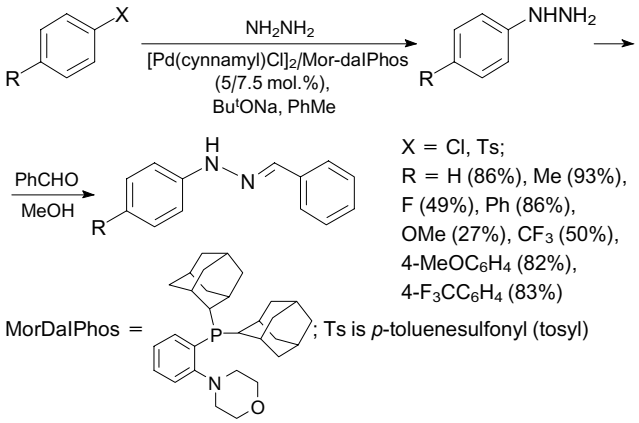
JosiPhos =



(R^3 = Ph, Cy; R^4 = Cy, Bu^t)

amination was carried out not only for aryl bromides and iodides, but also for (hetero)aryl tosylates. The range of nitrogen-containing reagents was also broad: amines, amides, imines and hydrazones.[42 – 44] Using MorDalPhos as the ligand, arylation was carried out for problem compounds such as ammonia[44] and hydrazine (in the latter case, the intermediate arylhydrazines were converted to more stable hydrazones),[45] and the yields of products largely depended on the nature of substituents in the aryl ring (Scheme 15).

Scheme 15

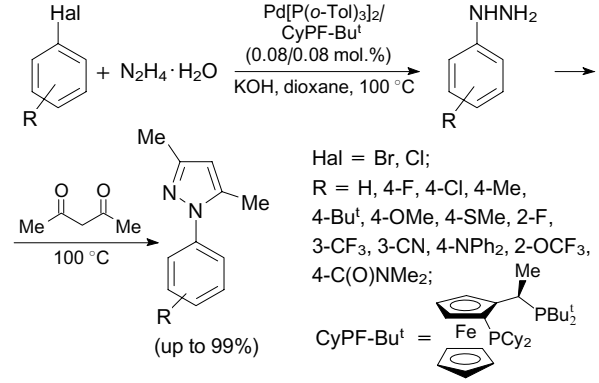


MorDalPhos =

; Ts is *p*-toluenesulfonyl (tosyl)

According to the results of the relatively few studies in this field,[46 – 48] palladium-catalyzed arylation of hydrazine is generally a fairly complicated task. However, recently it was found that as little as 0.08 mol.% of the Pd[P(*o*-Tol)$_3$]$_2$/CyPF-Bu^t catalytic system containing one of the JosiPhos ligands can be used for successive arylation of hydrazine

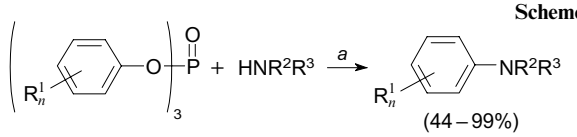
Scheme 16



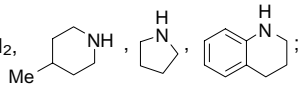
hydrate and subsequent *in situ* formation of substituted pyrazoles on treatment with acetylacetone.[49] A variety of aryl bromides and chlorides can participate in this reaction (Scheme 16).

Unexpectedly it turned out that the MorDalPhos ligand can be used for amination of triaryl phosphates; the product yields in many reactions of various amines exceeded 90% (Scheme 17).[50]

Scheme 17



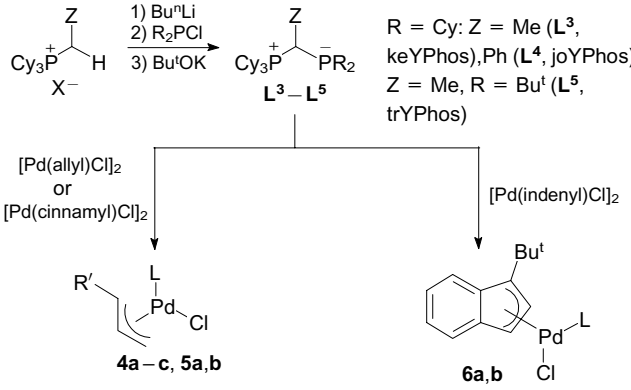
(*a*) [Pd(π-cynnamyl)Cl]$_2$/MorDalPhos (2/8 mol.%), K_2CO_3, CPME, 130 °C; R^1_n = H, 4-Me, 3,5-Me_2, 4-F, 4-CF_3, 4-OMe, 4-CN, 4-COPh, benzo[*b*], benzo[*c*]; HNR^2R^3 = $PhNH_2$, PhNHMe, 4-$PhC_6H_4NH_2$, 4-$AcC_6H_4NH_2$, 2-$PhC_6H_4NH_2$, 2,6-$Me_2C_6H_3NH_2$, 2,6-$Pr^i_2C_6H_3NH_2$, $BnNH_2$, 2-$FuCH_2NH_2$, 1-$NaphNH_2$,



CPME is cyclopentyl methyl ether, Fu is furyl, Naph is naphthyl

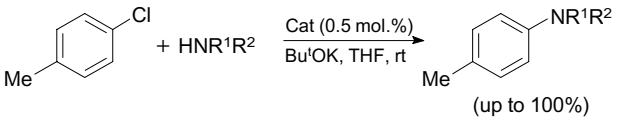
High efficiency in this reaction was found for a recently developed series of ylide-functionalized phosphines YPhos, which allow the amination to be carried out at room temperature.[51] The reactions involving palladium(II) allyl, cinnamyl or indenyl derivatives with the $\mathbf{L^3}-\mathbf{L^5}$ ligands (keYPhos, joYPhos and trYPhos, respectively) resulted in the isolation of eight palladium complexes. In the presence of compounds **4**–**6**, the test reactions of *p*-chlorotoluene with a number of primary and secondary amines gave amination products in quantitative yields. Complex **6b** ($P_{ind}2$) with joYPhos proved to be most efficient (Scheme 18).

Scheme 18



R′ = H: L = keYPhos (**4a**, $P_{al}1$), joYPhos (**4b**, $P_{al}2$), trYPhos (**4c**, $P_{al}3$);
R′ = Ph: joYPhos (**5a**, $P_{cin}2$), trYPhos (**5b**, $P_{cin}3$)

L = keYPhos (**a**, $P_{ind}1$), joYPhos (**b**, $P_{ind}2$)



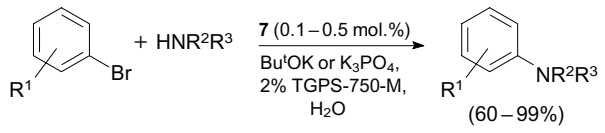
HNR^1R^2 = PhNHMe, Bu^nNH_2, Bu^tNH_2, Pr^iNH_2, Et_2NH, $PhCH_2NH_2$,



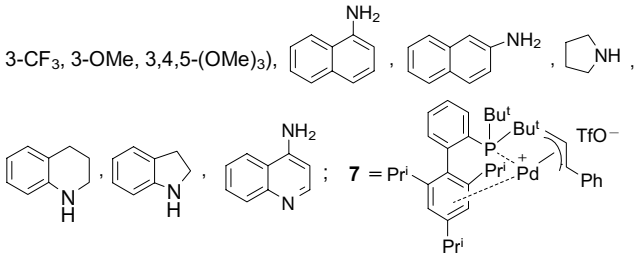
(P$_{ind}$2) with joYPhos proved to be most efficient (Scheme 18).

The possibility of performing reactions in water or in aqueous solutions has always been of interest for researchers, despite the limitations related to the poor water solubility of organic compounds; this is also true for palladium-catalyzed cross-coupling reactions.[52] In this case, two-phase systems with phase transfer catalysts are used, or reactions are carried out in microemulsions. Lipshutz and co-workers [53] reported reactions of aryl bromides with a large number of secondary cyclic, aromatic and heteroaromatic amines in aqueous solutions catalyzed by the palladium complex [Bu^{t}XPhosPd(cinnamyl)]OTf (**7**) in the presence of D,L-α-tocopherol methoxypolyethylene glycol succinate (TGPS-750-M) as the micelle-forming agent. The amination products were formed in high yields under these conditions even with minor amounts of the catalyst (approximately 0.1 mol.%) (Scheme 19).

Scheme 19

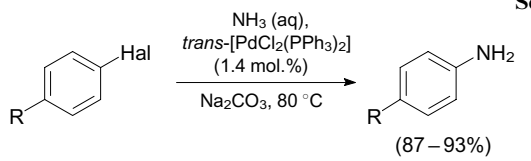


R^1 = 4-OMe, 3-OMe, 4-Ac, 3-Ac, 4-CO_2Et, 4-CF_3;
HNR^2R^3 = $X_nC_6H_{5-n}NH_2$ (X_n = 4-Me, 4-F, 4-Cl, 4-NO_2, 3-F, 3-CF_3, 3-OMe, 3,4,5-$(OMe)_3$),



An important amination reaction of aryl halides is the reaction of ArHal with ammonia to give anilines.[54] Initially, the catalytic synthesis of N-aryl-substituted benzophenone imines was used to introduce an amino group into aromatic compounds.[55] Later, methods involving directly ammonia were developed. These reactions were successfully carried out using aqueous ammonia [28] and lithium amide,[56] but the reaction with gaseous ammonia was also actively studied. In this case, the reaction conditions and the outcome are determined to a large extent by the ligand in the palladium complex.[57, 58] When the goal is to prepare anilines, it is necessary to exclude the reaction of the formed amine with aryl halide. Recently it was shown that the reactions with aryl bromides or aryl iodides with an aqueous solution of ammonia catalyzed by the palladium complex *trans*-[$PdCl_2(PPh_3)_2$] and conducted without an organic solvent

Scheme 20

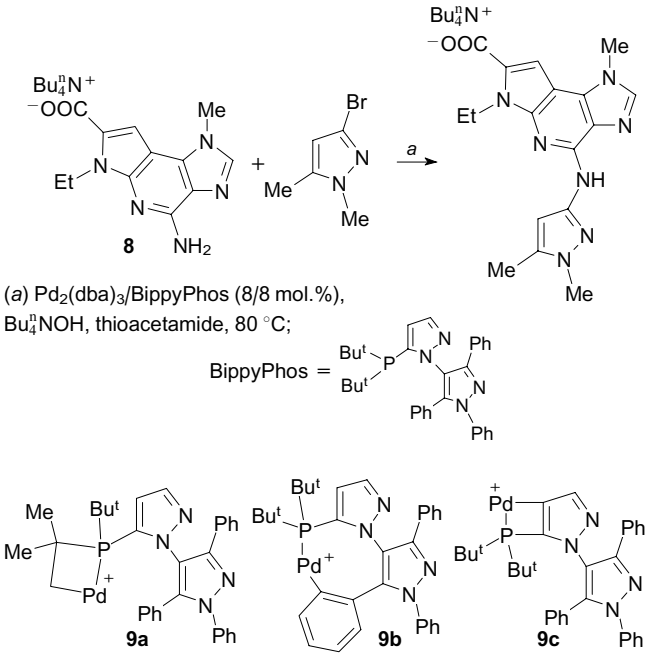


Hal = Br, I; R = H, Me, OMe, CHO, CN, NH_2, NO_2

give rise to the corresponding anilines in high yields (Scheme 20).[59]

In view of the fact that interest in studying the reaction mechanism has now markedly decreased, note the publication of Eastgate and co-workers,[60] who made an attempt to gain an insight into the cause of $Pd_2(dba)_3$/BippyPhos catalyst deactivation. The use of this catalyst was due to the necessity of arylation of the heteroaromatic amino acid salt **8**. It is known that palladacycles are reservoirs for catalytically active species and that some palladacycles may be very stable. The authors found out that the indicated ligand can form a stable cyclic compound with palladium, which eliminates the active metal from the catalytic cycle, thus decreasing the efficiency of catalysis (Scheme 21). Structures **9a** – **c** were proposed as the side palladacycles.

Scheme 21



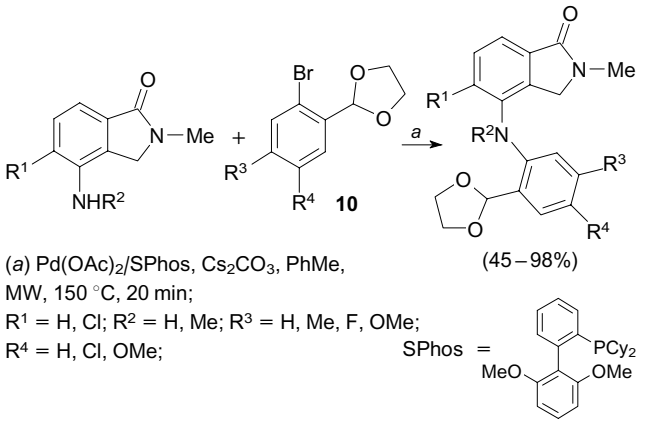
The amination of aryl halides is also performed using optimized procedures that are also used in other cross-coupling reactions, for example, microwave (MW) irradiation for acceleration of the process. We will present several examples of such reactions reported in recent years. The microwave-assisted reaction of protected 2-bromobenzaldehydes **10** with amines catalyzed by palladium acetate with SPhos ligand is completed within 30 min, with the product yields being in some cases up to 98% (Scheme 22).[61]

Brominated imidazo[2,1-*b*][1,3,4]thiadiazole **11** was subjected to microwave-assisted $Pd_2(dba)_3$/XantPhos-catalyzed amination reactions with several anilines, which gave the target products in up to 92% yields. However, when the aniline contained a *para*-trifluoromethyl group, the yield of the corresponding product decreased, while in the case of aliphatic amines (n-butyl- and benzylamines), the reaction did not proceed at all (Scheme 23).[62]

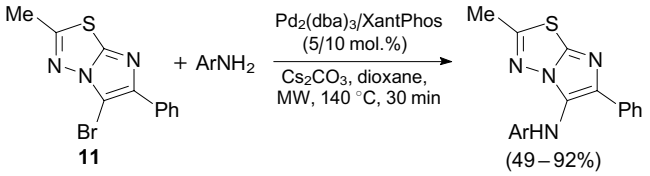
The use of microfluidic technique to carry out catalytic reactions of C – N bond formation in various compounds was addressed, in particular, by research groups of Buchwald and Kirschning.[47,63–65] In a recent study, Buchwald and co-workers [66] used palladium complexes with various phosphine ligands to study the reaction of *p*-tolyltrifluoromethanesulfonate with various N-nucleophiles (aniline, benzamide, 2-phenylethylamine and morpholine) in the presence of soluble organic compounds of different basicities (Scheme 24). AlPhos proved to be the most efficient ligand for amines, while BTTP showed the best properties as a base in the reactions with the most stubborn secondary dialkylamines.

In some cases, palladium-catalyzed amination is a step of one-pot synthetic procedures. For example, benzazepine, benzoxazepine and benzothiazepine derivatives **12** were obtained using a sequence of hydroaminoalkylation and palladium-catalyzed amination;[67] in the first step, titanium complex **13** acted as the catalyst, while the second step was catalyzed by the $Pd_2(dba)_3$/RuPhos system (Scheme 25).

Scheme 22

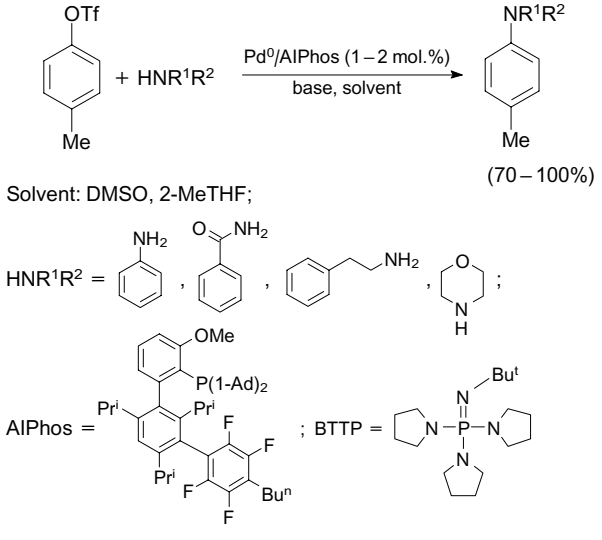


Scheme 23

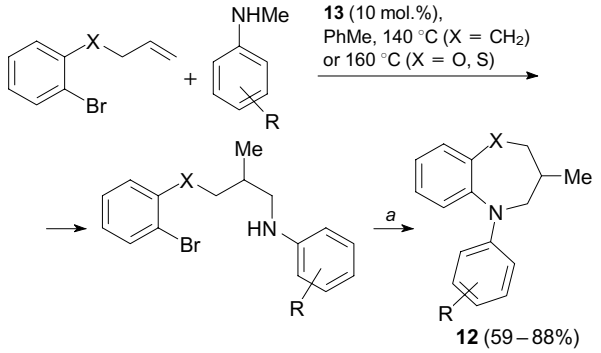


ArNH$_2$ = PhNH$_2$, 4-HOC$_6$H$_4$NH$_2$, 4-MeOC$_6$H$_4$NH$_2$, 2-MeOC$_6$H$_4$NH$_2$, 4-F$_3$CC$_6$H$_4$NH$_2$, 3,5-Cl$_2$C$_6$H$_3$NH$_2$

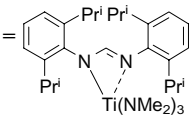
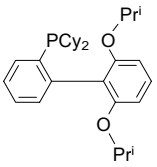
Scheme 24



Scheme 25

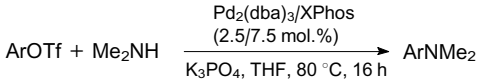


(*a*) $Pd_2(dba)_3$/RuPhos (2.5/7.5 mol.%), Bu^{t}ONa, PhMe, 110 °C;
X = CH_2, O, S; R = H, 4-Me, 4-OMe, 4-F, 4-OCF_3, 4-Pr^i, 4-Cl, 4-SMe, 3-Me, 3-F;

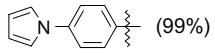
13 =  ; RuPhos = 

The introduction of aryl triflates instead of aryl halides into this reaction was described by Hartwig and co-workers [68] back in 1997. Since then, this method has often been used for the synthesis of arylamines, which was reflected in the reviews mentioned above.[2–4] Quite a recent publication [69] describes an elegant procedure for the preparation of diverse *N*,*N*-dimethylanilines in excellent yields from the appropriate aryl triflates and dimethylamine used as a solution in THF in the presence of the $Pd_2(dba)_3$/Xphos catalytic system (Scheme 26).

Scheme 26

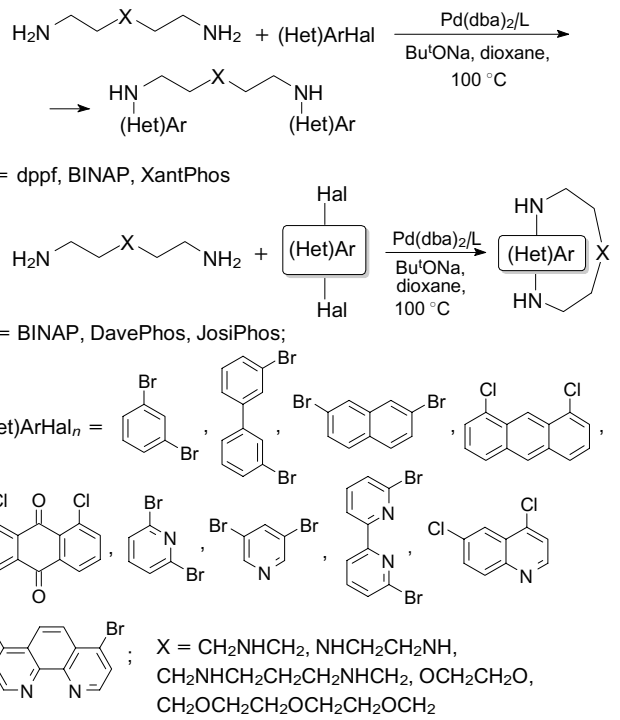


Ar = 4-XC_6H_4 (X = H (99%), Me (90%), Pr^i (90%), Bu^t (99%), OMe (92%), SMe (99%), NO_2 (71%), Ph (99%)), 2-Naph (95%),

 (99%)

We made a contribution to the development of palladium-catalyzed amination by studying some aspects of arylation and heteroarylation of di- and polyamines (oxadiamines and tri-, tetra-, penta- and hexaamines), such as the selectivity of substitution at a primary amino group in the presence of a secondary one; the possibilities of mono-, di- and tetra-arylation of di- and polyamines; dependence of the yields of products on the nature of the (hetero)aryl halide and the polyamine structure. We showed [70,71] that the $Pd(dba)_2$/BINAP system is, most often, the catalytic system of choice for amination and that the reaction is highly selective for polyamines, in which only primary amino groups are arylated, while almost no arylation of secondary dialkylamino groups is observed. The use of electron-donor phosphines, *e.g.*, DavePhos or JosiPhos, provides more efficient catalytic diamination of dihalo(hetero)arenes in problem cases. This enables the use of linear polyamines for the synthesis of polyazamacrocyclic compounds comprising various aromatic and heteroaromatic moieties, in particular those possessing the properties of chromophores and/or fluorophores (naphthalene, quinoline, anthraquinone, anthracene, bipyridine) (Scheme 27).[72–74]

Scheme 27

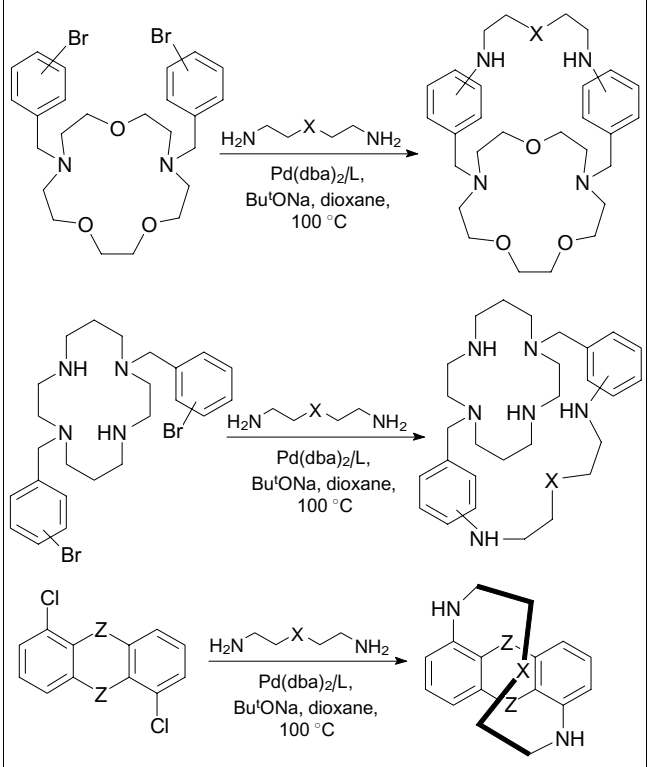


This methodology was extended by developing approaches to macropolycyclic compounds of various topology (for example, cryptands) [75] and by the synthesis of complex polyporphyrin systems and porphyrin conjugates with other macrocycles.[76,77] The use of chiral JosiPhos ligand made it possible to obtain planar chiral macrocycles from 1,5-dichloroanthraquinone and 1,5-dichloroanthracene with a moderate enantioselectivity: the enantiomeric excess (*ee*) for anthraquinone derivatives was 60% (Scheme 28).[78,79] Currently, the attention is focused on the use of palladium-catalyzed amination for the synthesis of fluorescent chemosensors for metal cations [80–86] and chiral organic molecules.[87–91] In particular, Scheme 28 gives examples of the preparation of macrobicycles based on diazacrown ethers and tetraazamacrocycles.[75]

Aromatic amines are widely used in both fundamental and applied research. The aminophenyl moiety is encountered in numerous natural compounds, pharmaceutical agents and compounds used in agrochemistry, in biological studies and for the design of new materials.[1] Among the latest achievements in the field of palladium-catalyzed amination, mention should be made of the key steps of synthesis of 7-isovaleryloxy-8-methoxygirinimbine and furoclausine B, containing carbazole as the central moiety.[92,93] A fused tetracyclic compound, azaborinine derivative, was also prepared according to this methodology;[94] this product is valuable for the design of optoelectronic systems. The Buchwald – Hartwig amination was also utilized for the synthesis of other polyfused systems with unusual electronic properties [95] and macrocyclic paracyclophanes containing a 9,10-diaminoanthracene moiety.[96]

In a multistep synthesis of new efficient complexing agents for the liquid – liquid extraction of minor actinides,

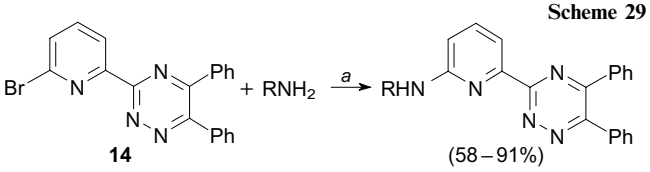
Scheme 28



L = BINAP, DavePhos, JosiPhos; X = CH_2NHCH_2, $NHCH_2CH_2NH$, $CH_2NHCH_2CH_2CH_2NHCH_2$, OCH_2CH_2O, $CH_2OCH_2CH_2OCH_2CH_2OCH_2$; Z = CH, C(O)

palladium catalysis and the CyPF-Bu^t ligand (JosiPhos series) were used in the step of amination of 1,2,4-triazine **14** (Scheme 29).[97]

Scheme 29

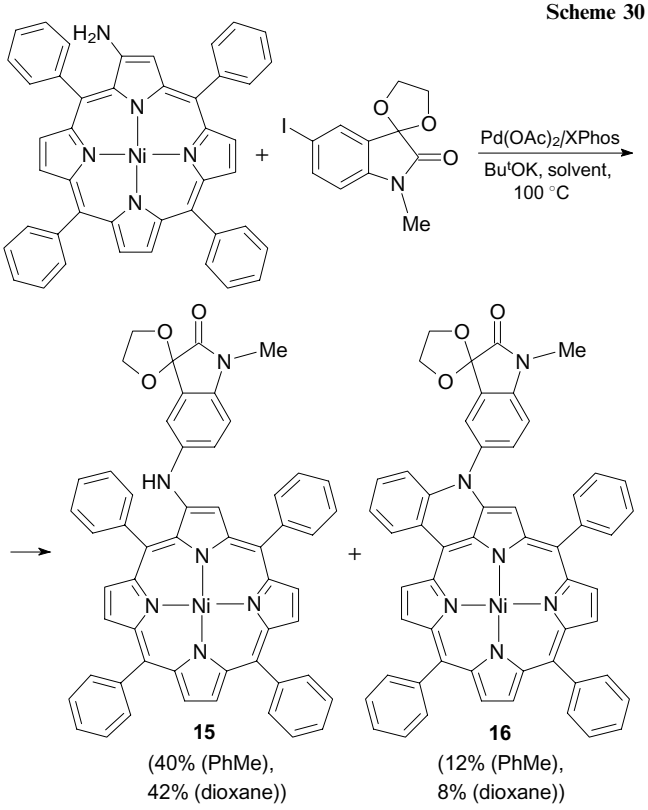


(*a*) Pd(dba)$_2$/CyPF-Bu^t (2.5 – 5/5 – 10 mol.%), K_3PO_4, PhMe, 100 °C; R = iso-C_5H_{11}, n-Hex, n-Oct, n-$C_{14}H_{29}$, $MeO(CH_2)_3$, 4-$XC_6H_4CH_2$ (X = H, Me, OMe), $Ph(CH_2)_2$, 3-$PyCH_2$, 2-$FuCH_2$

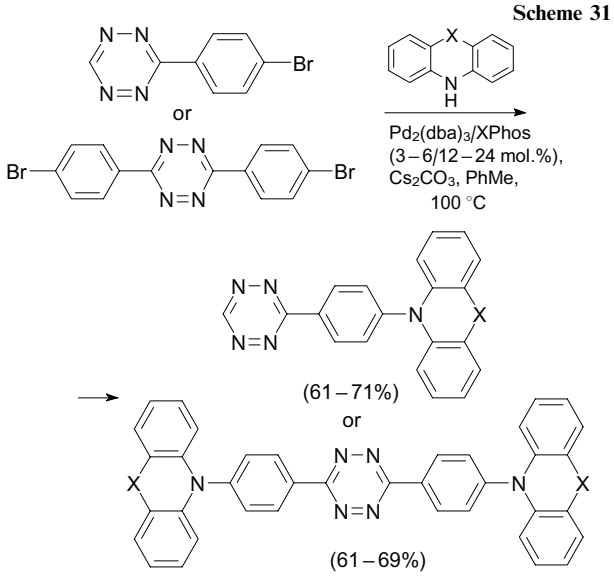
The reaction of porphyrin complexes with isatin was used to prepare new dyes and pigments.[98] In this case, a reactant is the amino derivative of the nickel tetraphenylporphyrin complex, the catalyst is palladium acetate with XPhos ligand, and the major product is complex **15**. Polycyclic compound **16** was isolated as a minor product, formed from the major product *via* intramolecular CH/NH amination, which is also catalyzed by $Pd(OAc)_2$ (Scheme 30).

Fluorescent chemosensors of the off/on type based on substituted 1,2,4,5-tetrazines were synthesized by palladium-catalyzed amination of appropriate *p*-bromophenyl derivatives. The reactions were carried out in the presence of the Pd(dba)$_2$/Xphos catalytic system and gave the target mono- and diamination products in good yields (Scheme 31).[99]

Scheme 30



Scheme 31



X = CMe_2, O, S

2.3. The use of palladium carbene complexes

N-Heterocyclic carbenes (NHC) were included into the list of most efficient ligands for palladium-catalyzed amination somewhat behind phosphine ligands, but their practical implementation started very rapidly; the fundamental role in the development of these ligands belongs to Organ and co-workers [100] and Bastug and Nolan.[101] Palladium NHC complexes can contain a palladacycle [102] or a labile pyridine ligand (so-called 'pyridine-enhanced precatalyst preparation stabilization and initiation', PEPPSI, family) (Fig. 3).[103]

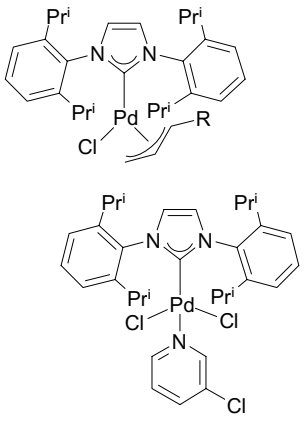
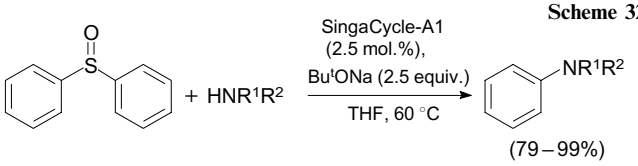


Figure 3. Palladium NHC-complexes including PEPPSI family.

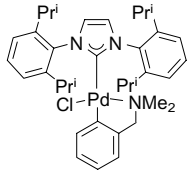
These ligands allow for further expansion of the range of substrates and for milder reaction conditions for amination: even for non-activated aryl chlorides, the reactions proceed at room temperature over short periods of time. In some cases, relatively small structural changes in complexes, for example the replacement of the allyl ligand by acetylacetone group, induce considerable changes in the catalyst activity, thus providing reactions of sterically encumbered (hetero)-aryl chlorides.[104] Further modification of ligands of the PEPPSI family may represent immobilization on a polymer support[105] and mechanochemical activation,[106] which expands the scope of catalytic amination. It is known that an important role for these reactions belongs to the leaving group (halogen or pseudo-halogen atom). The applicability of sulfide or sulfoxide groups for this role was studied. The use of NHC-containing palladacycle SingaCycle-A1 enables successful amination of diaryl sulfoxides (Scheme 32).[107]

Scheme 32

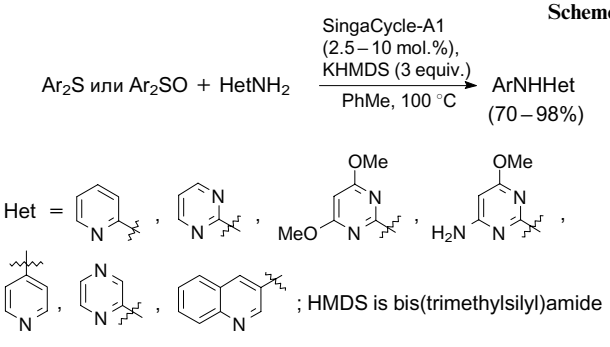


R^1 = 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-OHC_6H_4, 4-$MeSC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 3-$F_3CC_6H_4$, 2,6-$Me_2C_6H_3$; R^2 = H, Me, n-Hex, Cy, Bu^t, Bn;

SingaCycle-A1 =



Scheme 33



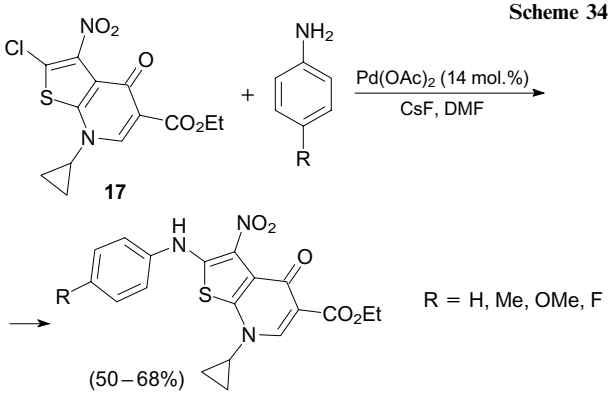
; HMDS is bis(trimethylsilyl)amide

The reactions with aromatic and heteroaromatic amines in the presence of this catalyst proceed under relatively mild conditions and give products in high yields (Scheme 33).

2.4. Reactions involving ligand-free palladium and heterogeneous and heterogenized palladium catalysts

It is known that the use of palladium salts in the absence of ligands as catalyst precursors gives rise to palladium nanoparticles (Pd-NPs) stabilized by a solvent and halide ions. It is for this reason that palladium-catalyzed reactions could formerly be carried out in water or aqueous organic mixtures in the presence of so-called ligand-free palladium, but usually with participation of aryl iodides. In a publication of 2019,[108] chlorinated thieno[2,3-*b*]pyridinone **17** was aminated with anilines using $Pd(OAc)_2$ as the catalyst in a high concentration in DMF to obtain products in good yields (Scheme 34). However, the possibility of this reaction is related to the use of caesium fluoride as a co-catalyst.

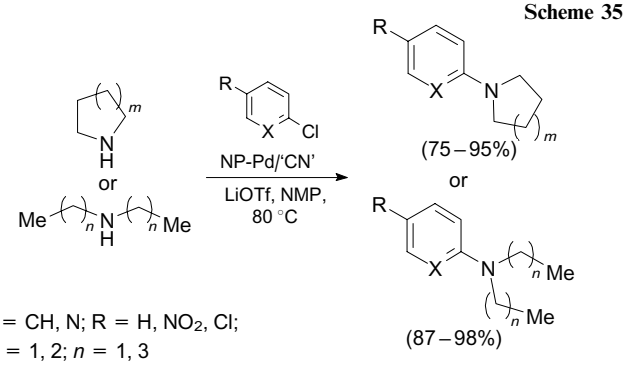
Scheme 34



A special place among cross-coupling reactions is occupied by the reactions carried out without ligands. In this case, palladium nanoparticles supported on various materials serve as the catalyst. Advantages of this catalyst include easy separation from reaction products and remaining reactants and the possibility of using lower catalyst amounts. An example of this type of catalysis in the aromatic amination is provided by the reaction of (hetero)-aryl chlorides with acyclic (Et_2NH, Bu^n_2NH) and cyclic (piperidine, pyrrolidine) secondary amines in the presence of the Pd-NP/'CN' system ('CN' is carbon nitride) and an unusual base, lithium triflate in *N*-methyl-2-pyrrolidone (NMP). This reaction resulted in the formation of expected products in high yields (Scheme 35).[109]

Karvembu and co-workers[110] reported the development of a simple and efficient catalyst for the arylation of aniline

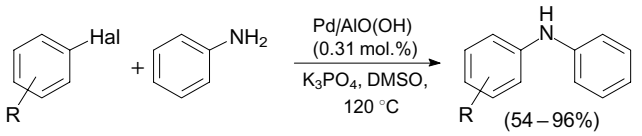
Scheme 35



X = CH, N; R = H, NO_2, Cl;
m = 1, 2; *n* = 1, 3

with various bromo- and chloroarenes. The catalyst was prepared by immobilizing Pd NPs (< 10 nm size) on nanoporous AlO(OH). The reactions proceeding in the presence of 0.31 mol.% Pd/AlO(OH) in DMSO at 120 °C with potassium phosphate as a base gave a variety of diphenylamines with substituents in one of the rings (Scheme 36) in moderate to nearly quantitative yields, in particular, for the amination of aryl chlorides. The catalyst retained the activity for up to four reaction cycles. Glorius and co-workers [111] noted that the Pd/Al_2O_3 catalyst, which is generally unreactive towards amination, can be activated by adding known N-heterocyclic carbenes as complexes with tetrafluoroboric acid; in this case, the reaction of some *para*- and *ortho*-substituted bromobenzenes with aniline gives the corresponding diphenylamines in up to 95% yield.

Scheme 36



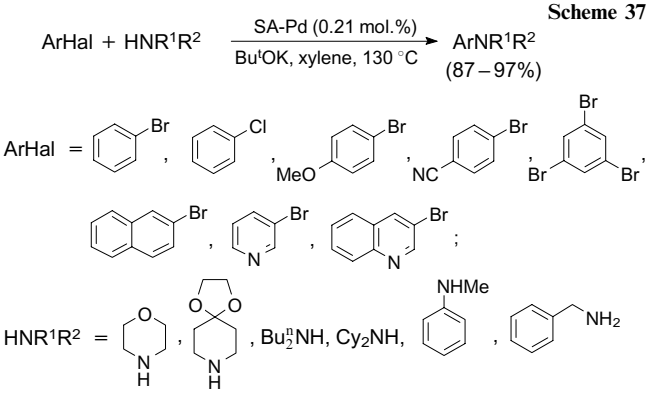
Hal = Br, Cl; R = H, 4-Me, 4-CF_3, 2-CN, 4-CN, 2-CHO, 4-CHO, 2-Ac, 4-CO_2H

The modification of carbon nanotube walls with di(2-sulfanylethoxy)triazines allowed for immobilization of palladium nanoparticles;[112] the MWCNTs/CC-SH/Pd catalyst obtained in this way proved to be efficient for the amination of aryl halides. The reactions with 0.5 mol.% catalyst were carried out in DMF at 100 °C; the best product yields (96%) were obtained in the amination of iodo- and bromobenzenes with morpholine and piperidine, while recycling experiments demonstrated that the catalyst retains the activity up to the seventh catalytic cycle.

The palladium nanoparticles immobilized on the magnetic iron particles coated by oleic acid (Fe@OA-Pd) proved to be efficient in the amination of aryl bromides and aryl chlorides with piperidine.[113] The best product yields were attained in the case of 1-bromo- (95%) and 1-chloronaphthalenes (90%) in the presence of 1.5 mol.% catalyst in a toluene – water mixture (5 : 1) at 105 °C.

Impressive results were obtained when palladium supported on sulfur-modified gold nanoparticles (SA-Pd) served as the catalyst.[114] Rather low catalyst loadings (0.21 mol.%) provided high yields of the products of amination of aryl bromides (87 – 97%) and even chlorobenzene (up to 93%) (Scheme 37). A thorough study of catalyst recyclability carried out for each reaction showed that the catalyst fully retains its activity even in the tenth cycle.

Scheme 37



3. Amination of aryl and heteroaryl halides catalyzed by copper complexes

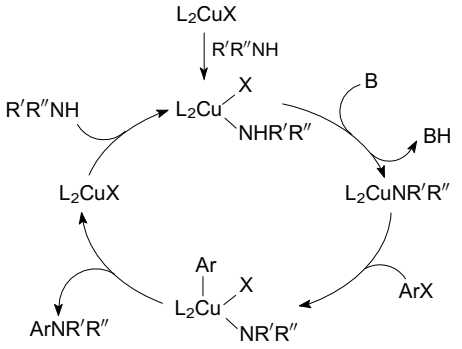
The reaction of C(sp^2) – N bond formation catalyzed by various copper salts has a long history and is connected with the names of Ullmann [115, 116] and Goldberg,[117] who were the first to perform this reaction at the dawn of the 20th century. These reactions have a high industrial value, first of all, for the production of dyes; however, the conditions of synthesis of the products were initially drastic. The optimization problem started to be solved with the use of nitrogen-containing bases, which simultaneously served as ligands for the catalyst. It was also important to choose an appropriate solvent, which contained water to dissolve copper compounds. As a result, this reaction was accomplished using a catalytic amount of copper, although this amount still noticeably exceeded the applied concentrations of palladium catalysts. It is evident that a relatively cheap method for the preparation of N-aryl-substituted compounds, especially heterocyclic ones, would possess a large synthetic potential for the development of drugs and new materials for electronics. There are examples demonstrating a higher efficiency of copper catalysis in comparison with the palladium or nickel catalysis, but they refer to specific cases of amination.[118] A major part of fundamental results on the copper-catalyzed amination were obtained in the first decade of the 21st century; therefore, the number of review publications on this subject is much smaller than that for palladium-catalyzed amination. Mention should be made of reviews of Ma and Cai [119] and Monnier and Taillefer,[120] published before 2010, which made a great contribution to the development of this field of chemistry. In the review published in 2011, Simas and co-workers [121] compared, in some cases, two alternative approaches: copper and palladium catalysis for amination of aryl halides. A general review [122] was published in 2014, while two other studies [123, 124] focused on the application of this method for the synthesis of natural compounds. Two book chapters and a monograph [125 – 127] devoted to this issue and a review [128] addressing particular aspects of amination appeared over the last decade.

The crucial role in the renaissance of the Ullmann reaction was played by ligands, which made the cross-coupling involving copper a catalyzed reaction. Among such ligands, mention should be made of N,N-, N,O- and O,O-ligands, which include amino acids, diamines, 1,10-phenanthroline, β-diketones, β-ketoesters, amides, 8-hydroxyquinoline and Schiff bases. The use of copper complexes with these ligands made it possible to change the conditions of the Ullmann reaction. Furthermore, by varying the structure of the ligand, it was possible to carry out the reactions at low temperature, down to room temperature, to decrease the amounts of copper and the ligand and to reduce the reaction time. This is especially noticeable for the amination reactions. However, no universal catalytic system for C(sp^2) – N bond formation has yet been found. The conditions should always be optimized and a particular ligand should always be chosen, depending on the nature of the aryl halide, especially on going from aryl iodides to aryl chlorides, and on the nature of the amine or amide. Moreover, this sensitivity to the ligand nature can be

followed even within the same family of similar substrates. The nature of the base also plays an important role.

The mechanism of the indicated reaction is studied rather actively, but the key issue related to the change in the copper oxidation state during the catalytic cycle has not yet been solved. The mechanism generally accepted for some time includes the exchange of the copper(I) salt anion with the nitrogen-containing nucleophile ($R'R''N^-$) and subsequent usual oxidative addition giving Cu^{III} and reductive elimination, resulting in the formation of the product and regeneration of the catalyst (Scheme 38).

Scheme 38

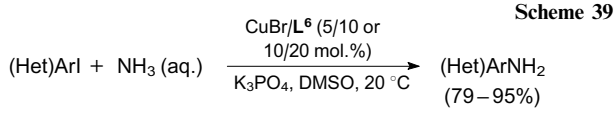


However, it cannot be ruled out that the sequence of steps in the catalytic cycle can be different. A more complex situation occurs in the case of catalysis by Cu^0 complexes in which the $Cu^0 \rightleftarrows Cu^{II}$ transition can take place in the catalytic cycle, instead of the $Cu^I \rightleftarrows Cu^{III}$ transition considered above. Morarji and Gurjar [129] proved that the outer-sphere single-electron transfer corresponding to the $Cu^I \rightleftarrows Cu^{II}$ transition may take place under certain conditions. This mechanism was proved for the reaction of chlorobenzene with aniline in the presence of the Cu^I/*N*,*N*′-bis(2,4,6-trimethoxyphenyl)oxalylamide catalytic system.

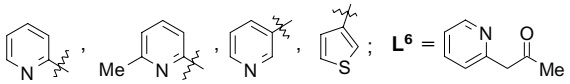
3.1. Copper-catalyzed arylation of ammonia

The synthesis of primary amines (aliphatic, aromatic and heteroaromatic ones) is in fairly high demand, because they serve as the starting compounds for the synthesis of pharmaceuticals, agrochemicals, organic dyes and materials for electronics. The application of copper salts and complexes in cross-coupling reactions to give the C – N bond proved to be rather successful,[130] in particular, for the synthesis of anilines from ammonia, and various procedures for conducting this reaction were proposed. The reaction of (hetero)aryl iodides and bromides with aqueous ammonia in the presence of ligand **L**^{6}, selected from a series of analogous compounds, gave high yields of products at room temperature (Scheme 39). *ortho*-Substituted aryl iodides were exceptions, requiring elevated temperature (80 °C).[131]

Scheme 39

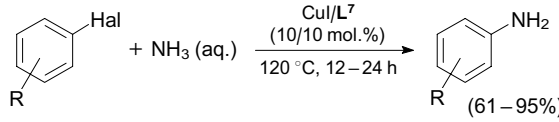


Ar = 4-RC$_6$H$_4$ (R = H, Me, Cl, OMe, Ac, CO$_2$Et, CN, NO$_2$);

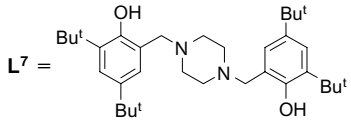
Het = 

The reaction with the use of CuI and diamine ligand **L**^{7} containing phenol substituents carried out at elevated temperature (120 °C) is equally successful (Scheme 40). Anilines are formed in up to 95% yields from aryl bromides and iodides.[132]

Scheme 40



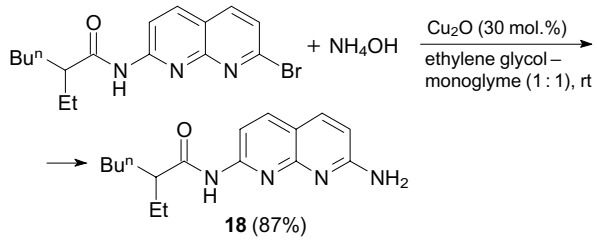
R = 4-Me, 4-NO$_2$, 4-Ac, 4-Cl, 3-Cl, 4-OMe, 2-OMe; Hal = I, Br;

L^7 = 

The reaction of aryl bromides and iodides with aqueous ammonia was carried out in the temperature range of 130 – 150 °C in DMSO, with the NH_3 to DMSO ratio being 3 : 1, or in PEG-300 in the presence of 1,2-dimethylethylenediamine and gave products in high yields. However, the competing hydrodehalogenation reaction often took place in parallel.[133]

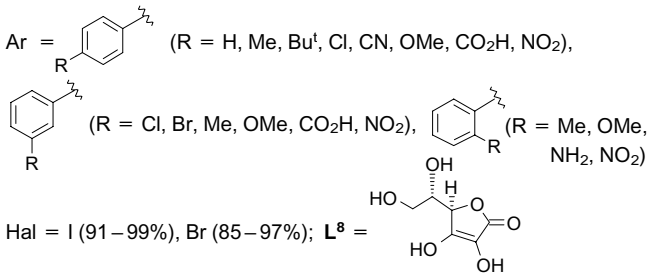
The introduction of the amino group for the synthesis of 2,7-diamino-1,8-naphthyridine derivative **18** was performed at room temperature in aqueous ammonia with Cu_2O as the catalyst without the addition of ligands (Scheme 41).[134] At first glance, copper oxides can be considered as heterogeneous catalysts; however, currently, the prevalent opinion is that in the presence of appropriate ligands, copper is washed away from the catalyst surface into the solution in the form of complexes, and the catalysis is actually homogeneous.

Scheme 41



The reaction of aryl halides ArHal (Hal = Cl, Br, I) with NH_3 was accomplished by using the CuI/ascorbic acid (AscH, **L**^{8}) catalytic system in liquid ammonia; it was possible to considerably decrease the amount of the catalyst (down to 1 mol.%).[135] The ligands that are normally used for Cu^I catalysis proved to be inefficient under these conditions; however, in the presence of ligand **L**^{8}, aryl bromides with various substituents were converted into the products in high or, in some cases, quantitative yields (Scheme 42). The reactions with aryl chlorides took place only if an electron-withdrawing group was present in the ring. Thus, chlorobenzene did not react with ammonia, while in the case of nitrochlorobenzenes, the yields of the corresponding anilines were 88, 63 and 74% for *ortho*-, *meta*- and *para*-isomers, respectively. The authors noted

Scheme 42

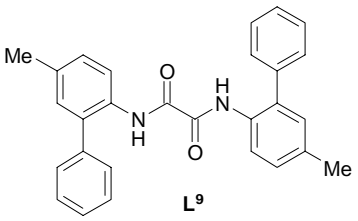


that even at 100 °C, no secondary arylation of the resulting anilines took place.

Similar results were observed using Cu_2O (equivalent amount) in ethylene glycol,[136] catalytic amount of Cu_2O,[137] CuI in the presence of L-proline in DMSO and H_2O, CuI in the presence of *trans*-4-hydroxyproline in DMSO, or $Cu(acac)_2$/**L**[7] (acac is acetylacetonate) in DMF.[138] Scalone and co-workers [139] used a similar precatalyst, and this reaction did not require the an additional ligand; probably, this function was performed by acetylacetonate. Attention is drawn by the fact that Cu^{II}, like Cu^{I}, serves as an excellent catalyst for the amination reaction.

Ma and co-workers [140] proposed oxalyl diamide **L**[9] as the ligand. Complexes with this ligand are able to catalyze the reaction of (hetero)aryl chlorides with ammonia.[141]

Structure L[9]



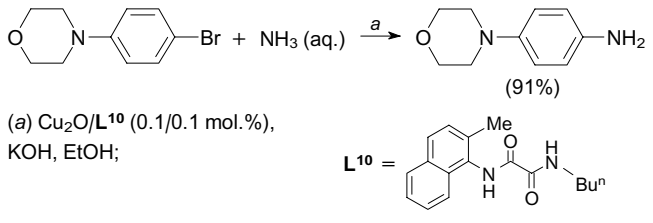
L[9]

A catalyst with structurally similar ligand **L**[10] (MNBO), in ethanol and in the presence of KOH as a base, provided successful reactions with ammonia for aryl iodides and bromides containing various substituents to furnish high yields of the corresponding anilines.[142] The reactions were conducted at 60 °C in the case of iodides and at 80 °C in the case of bromides, with loadings of both the copper catalyst (Cu_2O) and ligand **L**[10] being fairly low (0.1 mol.%) (for example, see Scheme 43).

3.2. Amine arylation by copper complexes

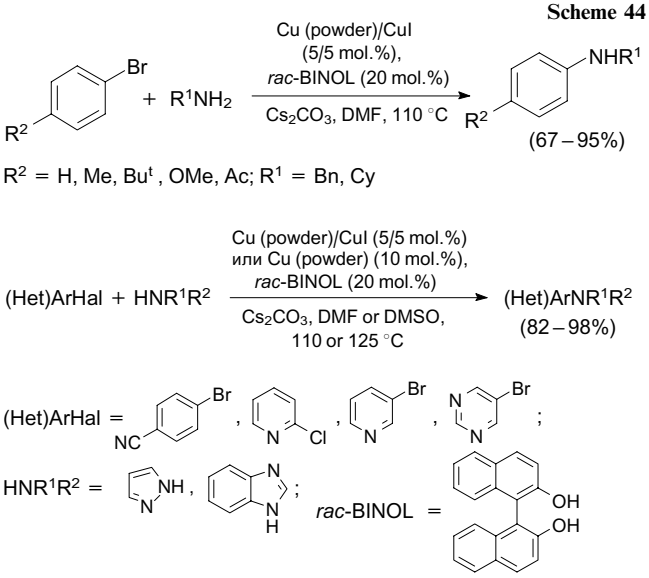
The copper-catalyzed formation of the N – C(Ar) bond was studied for a variety of NH-containing compounds; a fairly complete list of studies on this subject published before 2005

Scheme 43



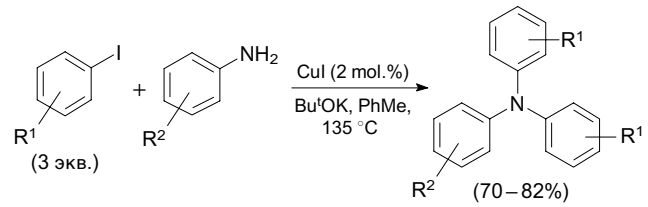
was reported by Wan and co-workers.[143] The authors of that study [143] carried out reactions of cyclic and acyclic aliphatic amines and heteroaromatic amines (pyrazole, benzimidazole) with aryl bromides using the Cu (powder)/CuI mixed catalyst and *rac*-BINOL (BINOL is 1,1′-bi-2-naphthol) ligand and thus obtained the amination products in high yields (Scheme 44).

Scheme 44



We would like to note a paper [144] published in 2002, in which ligand-free copper iodide was introduced into the arylation of aromatic amines to give triarylamines in one step (Scheme 45). The addition of nitrogen-containing ligands such as 2,2′-bipyridine, terpyridine, phenanthroline and its derivatives may increase the yield of triarylamines up to 90 – 95%.

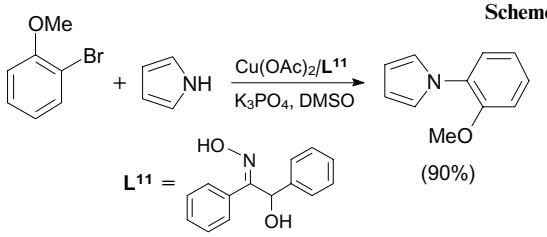
Scheme 45



The arylation of pyrrole was carried out using the $Cu(OAc)_2$/**L**[11] catalytic system in DMSO in the presence of potassium phosphate.[145] Under these conditions, the reaction with *o*-bromoanisole gave the product in 90% yield (Scheme 46). Note that ligands that are normally used in copper-catalyzed reactions had low efficiency in this case. Imidazole and cyclic amines smoothly reacted with *o*-bromoanisole, and the reaction of diethylamine with bromobenzene gave the product in 92% yield. The authors assumed that the Cu^{I}-catalyzed reaction proceeds *via* the formation of Cu^{III}.

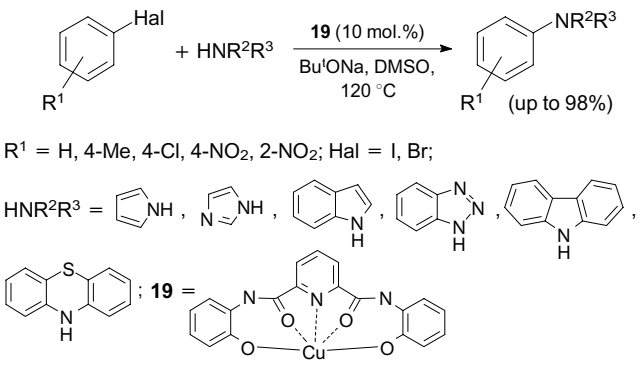
Copper(II)-based heterogeneous catalyst **19** was used in the amination of aryl halides; the reaction was carried out without a solvent or with a minimum amount of a solvent at 120 °C, with the product yields being up to 98%

Scheme 46



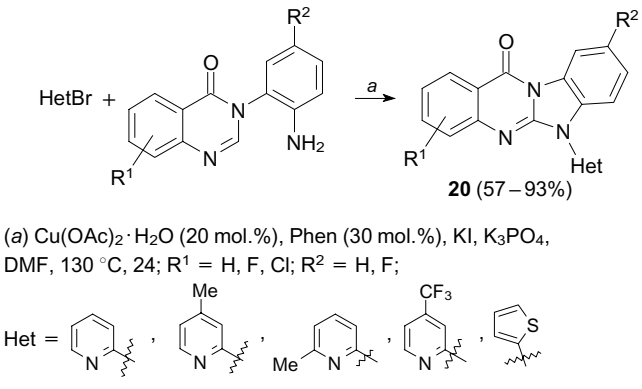
(Scheme 47). In the case of aliphatic secondary amines, the yields were modest: 45% for diethylamine and 65% for di-n-butylamine. Catalyst **19** can be recovered by mere filtration.[146]

Scheme 47



The amination – oxidative amination cascade reaction was used to link two biologically active moieties into one benzimidazoquinazolinone molecule **20** (Scheme 48). The reaction catalyzed by $Cu(OAc)_2 \cdot H_2O$ (20 mol.%) in the presence of 1,10-phenanthroline (Phen) as a ligand and potassium phosphate as a base could be accomplished if potassium iodide was added to the reaction mixture.[147]

Scheme 48



In order to arylate indole, Ma and Cai[119] studied the effect of the nature of amino acid on its ability to form a metal complex. The best result, determined by the ability to coordinate to copper, was found for methionine, which is coordinated *via* NH_2, CO_2H and S groups. In the presence of the CuI/amino acid system (10/20 mol.%), indole reacted with aryl halides containing various substituents to give products in good yields. In addition, aliphatic amines and morpholine were smoothly arylated, and the products were formed in 62 – 75% yields.

In 2002, Buchwald and co-workers[148] described the reaction of aryl iodides with primary alkylamines and cyclic secondary amines. The reaction was carried out under mild conditions: 5 mol.% CuI in isopropyl alcohol at 80 °C with potassium phosphate as a base, but at higher concentration of the ethylene glycol ligand (200 mol.%). A similar reaction was carried out for aryl bromides at 90 °C in the presence of ligand $\mathbf{L}^{12}$ (Fig. 4). With this ligand and more reactive aryl halides, it was possible to reduce the amount of CuI to 1 mol.%. Later, ligands $\mathbf{L}^{13}$ and $\mathbf{L}^{14}$ were proposed, and this made it possible to carry out amination at 25 °C for aryl iodides and at 90 °C for aryl bromides using 5 mol.% CuI and 20 mol.% ligand in DMF in the presence of caesium carbonate as a base.

Meanwhile, Ma and co-workers[149] showed that excellent results can be obtained by using amino acids — proline and *N*-methylglycine ($\mathbf{L}^{15}$) — in this reaction. Good catalytic performance was found for CuI complexes with ligand $\mathbf{L}^{16}$, which allowed the reactions for reactive aryl halides to be carried out at room temperature.[150] Using CuI/$\mathbf{L}^{15}$ and CuI/$\mathbf{L}^{16}$ systems and organic bases ([Alk_4N]OH or [Alk_4P]OH), Liu and co-workers[151] also carried out reactions with aryl bromides and iodides at room temperature. They showed that at high loadings of the catalyst (CuI complex with proline) in the presence of excess amine, amination is possible for a broad range of aryl iodides at room temperature.[152]

An important step towards improving the amination conditions was made by using 8-hydroxyquinoline *N*-oxide ($\mathbf{L}^{17}$) as a ligand, which made it possible to carry out the reaction with good product yields for diversely substituted aryl iodides and bromides and also for aryl chlorides with strong electron-withdrawing substituents at low concentrations of the catalyst and the ligand (1 mol.% CuI and 2 mol.% $\mathbf{L}^{17}$) in DMSO, at moderate temperatures (65 – 110 °C) and in the presence of caesium carbonate.[153] Finally, ligand $\mathbf{L}^{10}$, which has already been noted for the reactions with ammonia (see Scheme 43), allowed Ma and co-workers[142] to carry out an analogous reaction with primary amines using Cu_2O catalyst in concentrations that were exceptionally low for catalysis by copper complexes: 0.001 mol.% for aryl iodides (at 50 °C) and 0.01 mol.% for aryl bromides (at 80 °C). This reaction was scaled-up, and 4-methoxy-*N*-(n-butyl)aniline was obtained in 95% yield in an amount of 40 g at a time.

Provided that an appropriate ligand has been chosen, cyclic secondary amines are converted to the products in high, often quantitative yields. Ma and co-workers[154] used

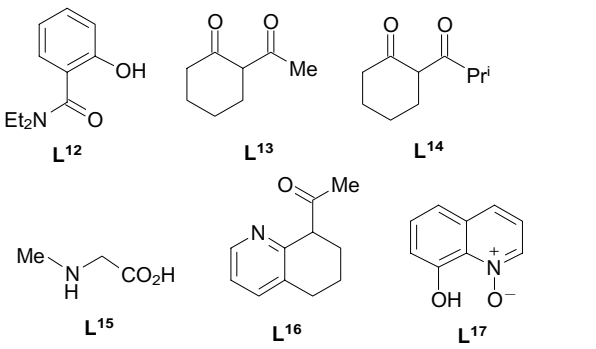
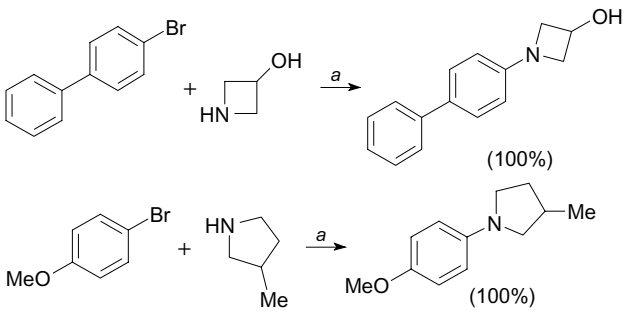


Figure 4. O,O- and N,O-Type ligands for copper-catalyzed amination.

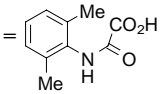
ligand **L**[18] to carry out the reactions of aryl iodides and bromides with aliphatic secondary amines; they obtained amination products in good to high yields. Examples of synthesized compounds are presented in Scheme 49.

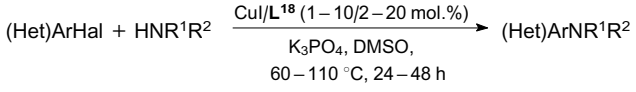
Scheme 49



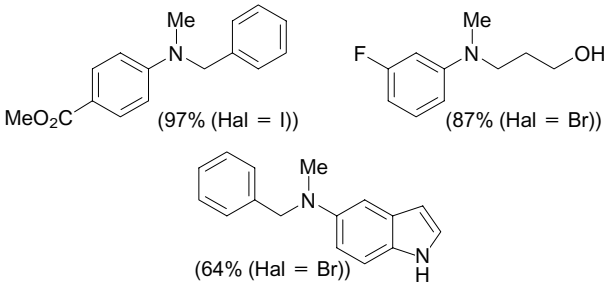
(*a*) CuI/**L**[18] (10/20 mol.%), K_3PO_4, DMSO, 110 °C;

L[18] =





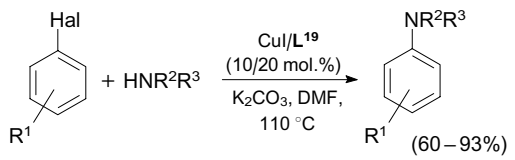
Examples of products



More nucleophilic and more sterically encumbered acyclic secondary amines are more difficult to aminate than primary or cyclic secondary amines; such reactions are not numerous.[155]

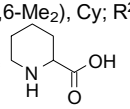
The preparation of diarylamines by this type of cross-coupling is fairly problematic and requires an approach differing from that described above. Fu and co-workers[156] carried out reactions of iodo- and bromobenzenes with anilines, cyclohexylamine and morpholine in the presence of ligand **L**[19] (Scheme 50), with product yields varying from good to high (60 – 93%). However, in the case of chlorobenzene, analogous amination reactions led to a modest result (15 – 31% yields).

Scheme 50



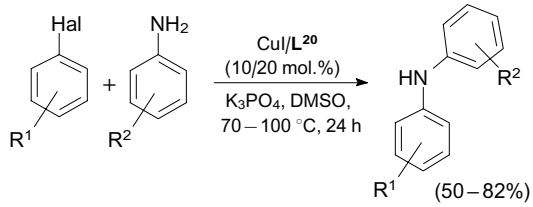
R^1 = H, 4-OMe; R^2 = H: R^3 = $X_nC_6H_{5-n}$ (X_n = H, 2-NO_2, 2-OMe, 2-CO_2H, 4-NO_2, 2,6-Me_2), Cy; R^2-R^3 = $(CH_2)_2O(CH_2)_2$; Hal = I, Br;

L[19] =



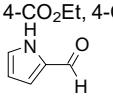
Buchwald and co-workers[157] used pyrrole-2-carbaldehyde (**L**[20]) as a ligand to carry out the reaction of aryl iodides and bromides with anilines, which gave very good results (Scheme 51). Apparently, this reaction is considerably affected by the nature of the base, since the reaction of iodobenzene with aniline can also be catalyzed by ligand-free copper iodide.

Scheme 51



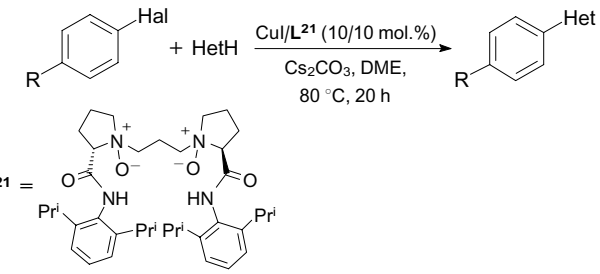
R^1 = H, 4-OMe, 4-SMe, 4-F, 4-Cl, 3-OMe, 3-CN, 3-CO_2Et, 2-OMe, 2-Me; R^2 = H, 4-F, 4-Me, 4-OMe, 4-Ac, 4-CO_2Et, 4-CN, 4-NHAc, 3-Me, 3-CF_3, 2-OMe; Hal = I, Br;

L[20] =



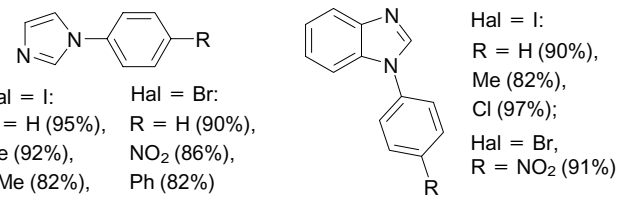
It is noteworthy that chiral N,O-ligands, which are normally used in asymmetric synthesis, were also introduced into the copper-catalyzed amination of aryl iodides and bromides with heteroaromatic amines.[158] Bis(pyrrolidine) *N*-oxide derivative **L**[21], containing bulky 2,6-diisopropylphenyl substituent, proved to be the most efficient ligand (Scheme 52).

Scheme 52



L[21] =

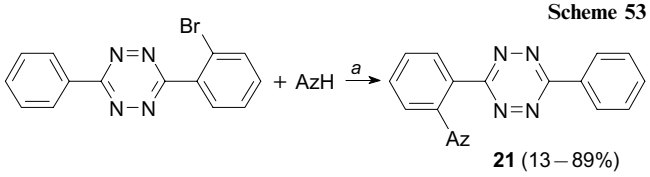
Examples of products



Interesting conjugates of diphenyltetrazine with azoles (AzH) (compounds **21**) were prepared with the standard copper catalyst CuI in the presence of a large amount of the TMEDA ligand (TMEDA is tetramethylethylenediamine). The replacement of the bromine atom in position 2 of the benzene ring resulted in different yields for different azoles: the yields varied from modest (13%) to high (80 – 89%) (Scheme 53).[159]

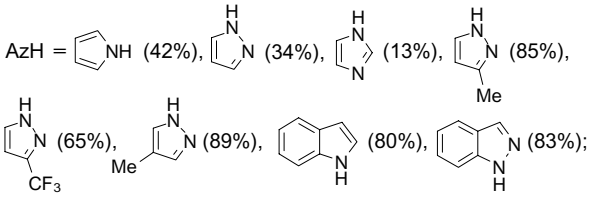
It was found that D-glucose efficiently reduces Cu^{II} to Cu^{I} during the amination of a broad range of substituted bromobenzenes, with product yields being, in some cases,

Scheme 53

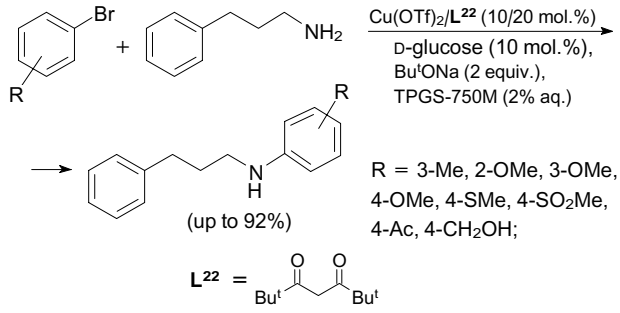


21 (13 – 89%)

(*a*) CuI (20 mol.%)/TMEDA (2 equiv.), K_2CO_3, PhMe, 90 °C, 16 h;

AzH =  (42%), (34%), (13%), (85%), (65%), (89%), (80%), (83%);

Scheme 54



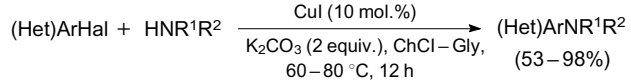
higher than 90%.[160] β-Diketone **L**[22] was the most efficient ligand (Scheme 54).

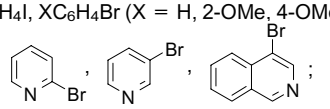
A method of ligand-free copper(I)-catalyzed amination in low-melting eutectic mixtures of choline chloride with glycerol (ChCl – Gly, 1 : 2 ratio) was proposed (Scheme 55).[161] In the case of aliphatic primary and secondary amines, it is sufficient to use potassium carbonate as a base at temperatures of 60 – 80 °C. When aniline is taken for the reaction, high (> 70%) yields of amination products can be obtained if the basicity of the medium is increased by using 3 equiv. of potassium *tert*-butoxide and the reaction is conducted at 100 °C. The possibility of reuse of the eutectic mixture for up to five cycles without a significant decrease in the yield of the cross-coupling product was shown using a separate example.

Our attention was focused on the study of the Cu^I-catalyzed arylation and heteroarylation of various adamantane-containing amines because of high potential physiological activity of these compounds. A series of publications [162 – 166] describe the characteristic features of reactions depending on the spatial environment of the amino group (the adamantane cage is a bulky substituent, which strongly influences the efficiency of substitution at the amino group) and on the structure of (hetero)aryl halide (the nature of the halogen atom, the presence of electron-donating or electron-withdrawing groups, and the substituents in the *ortho*-position relative to the halogen atom). We studied a variety of catalytic systems differing in both the source of copper and the nature of the ligand. The CuI complexes with *rac*-BINOL or 2-isobutyrylcyclohexanone (**L**[14]) ligand were found to be most efficient and provided the target products in yields exceeding, in some cases, 80% (Scheme 56). Certain limitations of this method were also demonstrated: for example, in the vast majority of cases, it is better to use iodo derivatives of benzene and pyridine, and considerable steric hindrance either at the amino group or the halogen atom sharply decrease the yields of (hetero)arylation products. The results of copper-catalyzed amination were compared with the data obtained for Pd^0-catalyzed reactions of the indicated adamantane-containing amines. The key advantage of the copper-catalyzed process is that the side N,N-diarylation reaction is substantially suppressed, which is especially important for reactions with more reactive halogen-substituted pyridines and quinolines.

One more line of research concerns copper(I)-catalyzed *N*,*N*′-di(hetero)arylation of linear diamines, oxadiamines and polyamines, including those with known biological activities (putrescine, cadaverine, spermine, spermidine, norspermine and norspermidine).[167 – 171] The regularities of

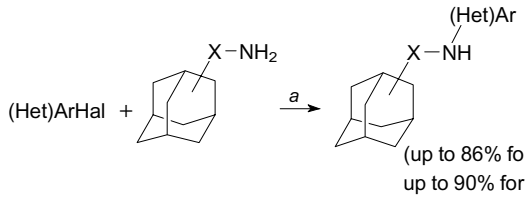
Scheme 55



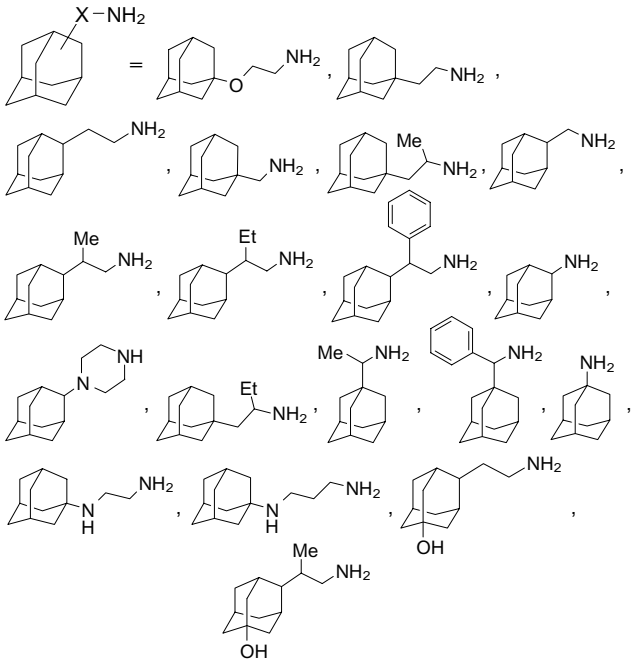
(Het)ArHal = 3-$MeOC_6H_4I$, XC_6H_4Br (X = H, 2-OMe, 4-OMe, 4-CN, 4-NO_2, 4-CO_2Et), ;

HNR^1R^2 = Bu^n_2NH, n-$HexNH_2$, $CyNH_2$, $Me_2N(CH_2)_2NH_2$, $Et_2N(CH_2)_2NH_2$, $Ph(CH_2)_2NH_2$, morpholine

Scheme 56



(*a*) CuI/*rac*-BINOL or **L**[14] (10 – 20/20 – 40 mol.%), Cs_2CO_3, DMF, 140 °C, 24 h; Hal = I, Br;



Scheme 57

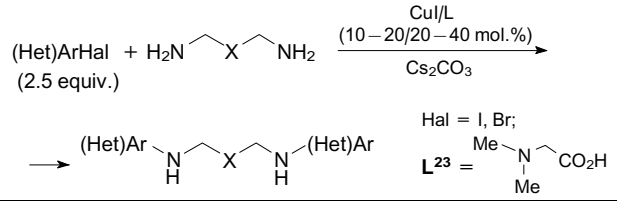


Table 1. *N*,*N*′-Di(hetero)arylation of linear di- and polyamines and oxadiamines.[172]

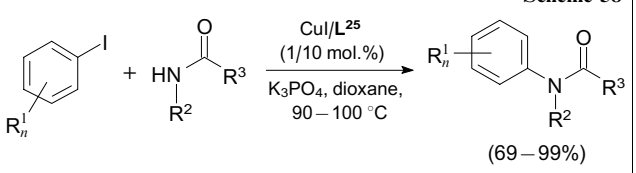
Amines	Conditions	Yields (%)	
		Ar	Het = Py
Diamines:			
X = $(CH_2)_n$ (n = 1 – 4, 8);	*rac*-BINOL or	up to 98	up to 79
Oxadiamine:	**L**[14], DMF,		
X = $CH_2O(CH_2)_2OCH_2$,	140 °C, 24 h		
$(CH_2)_2O(CH_2CH_2O)_2(CH_2)_2$,			
$(CH_2)_2O(CH_2)_4O(CH_2)_2$			
Polyamines:			
X = $(CH_2)_2NH(CH_2)_2$,	L-Pro or **L**[23],	up to 92	up to 75
$(CH_2)_2NH(CH_2)_3$,	EtCN, 110 °C,		
$CH_2NH(CH_2)_2NHCH_2$,	24 h		
$CH_2NH(CH_2)_3NHCH_2$,			
$(CH_2)_2(NHCH_2CH_2)_2$,			
$(CH_2)_2NH(CH_2)_3NH(CH_2)_2$,			
$(CH_2)_2NH(CH_2)_4NH(CH_2)_2$			

these reactions were elucidated. The above-indicated CuI/*rac*-BINOL and CuI/**L**[14] systems proved to be catalysts of choice for diamines and oxadiamines, while for most polyamines, the highest efficiency was observed for systems containing L-proline (L-Pro) or *N*,*N*-dimethylglycine (**L**[23]) (Scheme 57, Table 1). In some cases, the yields of products of the copper-catalyzed arylation of oxadiamines were comparable with or higher than the yields obtained using palladium catalysts, owing to the suppression of the side N,N-diarylation. However, the reactions of polyamines faced certain difficulties caused by arylation of secondary amino groups, which was especially noticeable for iodopyridines. The results of these studies were summarized in a recent review.[172]

3.3. Copper-catalyzed arylation of amides

The Goldberg reaction (arylation of amides), as a modification of the Ullmann – Goldberg reaction, is carried out under miler conditions. The catalyzed variant of this reaction was first accomplished in 2001 by Buchwald and coworkers[173] using 1,2-diamines as ligands. This reaction was carried out for aryl iodides, bromides and even chlorides in the presence of 1 mol.% CuI and 10 mol.% ethylene diamine (**L**[24]) or cyclohexane-1,2-diamine (**L**[25]) (Scheme 58, Fig. 5). Dioxane served as the solvent, while potassium phosphate or (in some cases) carbonate served as the base; depending on the nature of substituents in the starting compounds and on the halogen, the yields of products varied over a broad range from good to nearly quantitative. In the case of aryl iodides, only 1 mol.% CuI was most often required. In some reactions, it was shown that the catalyst amount may be decreased to 0.2 mol.%. When aryl bromides and, the more so, aryl chlorides were subjected to amidation, the amount of copper iodide had to be increased

Scheme 58



R^1_n = 4-OMe, 4-NH_2, 3,5-Me_2, 2-OMe, 2-NMe_2, 2-NO_2;
R^2 = H, Me, Ph; R^3 = H, Me, Ph, 4-$H_2NC_6H_4$

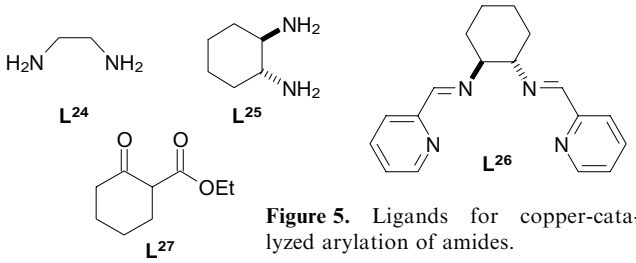


Figure 5. Ligands for copper-catalyzed arylation of amides.

to 5 – 10 mol.% and the temperature had to be raised to 110 – 130 °C; the product yields reached or even exceeded 90%.

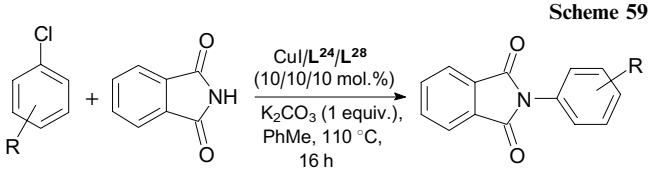
Subsequently, research groups headed by Taillefer[174] and Guo,[175] independently used new ligand **L**[26], which is a double Schiff base derived from cyclohexane-1,2-diamine and 2-pyridylcarbaldehyde, in the Goldberg reaction. Lv and Bao[176] proposed to carry out this reaction using O,O-ligand **L**[27], representing ethyl 2-oxocyclohexanecarboxylate (see Fig. 5), which was also successfully used for amidation of aryl iodides (at room temperature) and aryl bromides (at 80 °C), with the CuBr loading being 10 mol.% and the ligand **L**[27] concentration being 20 mol.%.

Recently, a series of reactions of substituted chlorobenzenes with simple amines and amides were carried out in order to find the optimal ligands and bases for amination and amidation.[177] A number of experiments demonstrated that the best yields in the amidation of chlorobenzenes are attained by the simultaneous use of two structurally very similar ligands: 1,2-ethylenediamine (**L**[24]) and its dimethylated derivative (**L**[28]). The yields of amidation products were considerably affected by both the nature and the position of substituent in the aromatic ring; no unique dependence was observed on either the electronic properties or steric hindrance of substituents at the chlorine atom (Scheme 59).

3.4. Cu^I-catalyzed arylation of NH-heterocycles

The arylation of NH-heterocycles is of interest for the synthesis of compounds with useful electronic and fluorescent properties. In this case, too, by using appropriate

Scheme 59



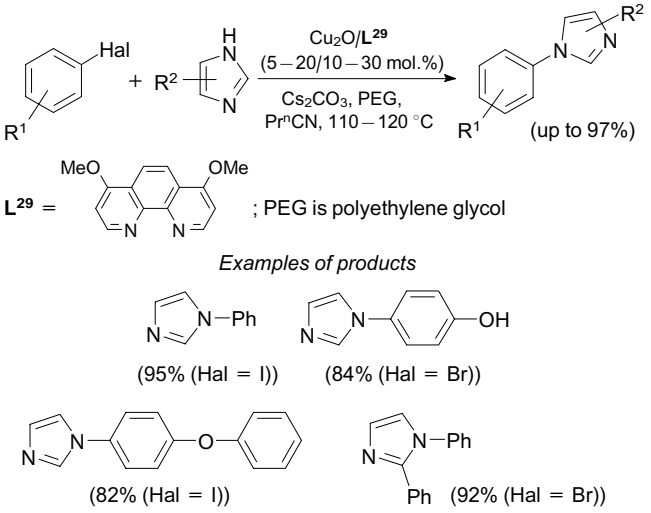
R = 4-NO_2 (82%), 3-NO_2 (96%), 2-NO_2 (0%), 4-CO_2H (86%), 2-CO_2H (99%), 4-Cl (60%), 4-NH_2 (92%), 4-Me (16%), 2-Me (15%);

L[28] = Me N N Me (H H)

bidentate ligands, it is possible to selectively perform the catalyzed variant of this reaction. The arylation of azoles possessing different acidity demonstrates most clearly that it is impossible to select a universal ligand that would efficiently perform the reaction for all representatives of this group of compounds. Almost every azole requires its own ligand that provides a high yield of product and makes it possible to carry out the reaction not only for aryl iodides, but also for aryl bromides. The choice of the ligand must be combined with other factors such as the natures of the base and the solvent, temperature and the character of the copper catalyst precursor. Currently, a great body of data has been accumulated, covering various types of ligands: diamines, phenanthroline and its analogues, amino acids, oxalic acid diamide and 8-hydroxyquinoline derivatives, which were tested for various series of azoles.

In 1999, Buchwald and co-workers [178] reported the N-arylation of imidazole, methylimidazole and benzimidazole with aryl iodides in the presence of a catalytic amount (10 mol.% copper) of the $(CuOTf)_2 \cdot PhH$ complex and a stoichiometric amount of 1,10-phenanthroline as a ligand. The reactions were carried out in xylene at 100–125 °C under the action of caesium carbonate and gave arylation products in 62 to 99% yields. It was found that aryl bromides also successfully react under these conditions. Later, the arylation of imidazoles with aryl bromide in the presence of 4,7-dimethoxy-1,10-phenanthroline (**L**[29]) was also carried out; the products were obtained in high yields at lower concentrations of the catalyst and lower temperatures (Scheme 60).[179]

Scheme 60

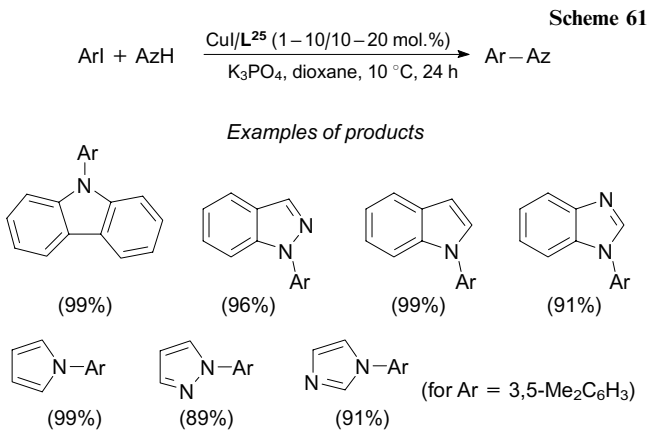


Even higher yields of arylation products were attained for a large series of azoles upon the CuI-catalyzed reaction with aryl iodides in dioxane in the presence of cyclohexane-1,2-diamine (**L**[25]) (Scheme 61).[173]

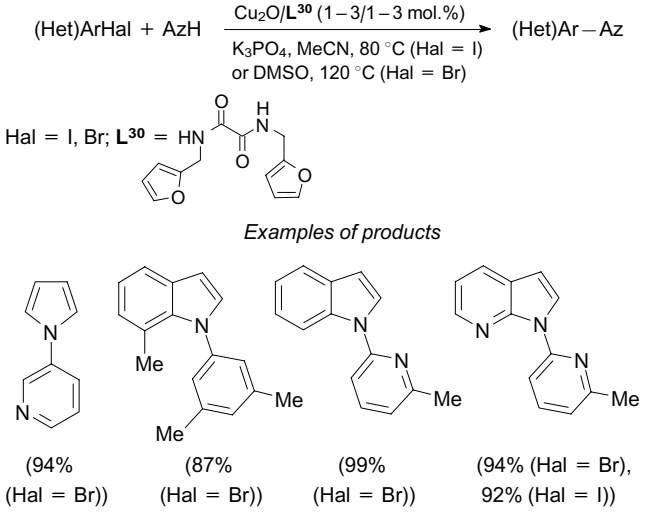
The BFMO ligand, *N*,*N*′-bis[(2-futyl)methyl]oxalamide (**L**[30]), derived from oxalic acid diamide, proved to be efficient in the reactions of aryl and heteroaryl halides with diverse azoles.[180] When only 1–3 mol.% Cu_2O and the same ligand concentrations were used, the reactions gave high yields of products (Scheme 62).

Even minor changes in the ligand structure can induce pronounced changes in the catalytic action. Thus the use of 2-methyl-8-hydroxyquinoline (**L**[32]) and 8-hydroxyquinoline

Scheme 61

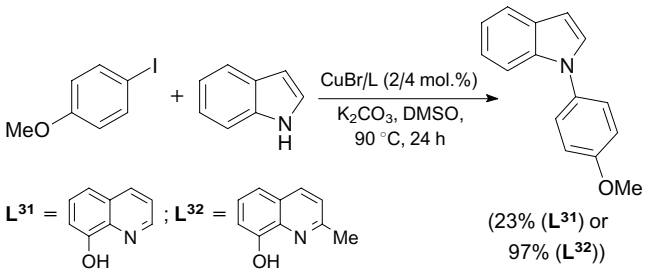


Scheme 62



N-oxide (**L**[17]),[153] instead of usual 8-hydroxyquinoline (**L**[31]), sharply increased the yield of products of amination of *p*-iodoanisole with indole and decreased the reaction temperature to 90 °C (Scheme 63).

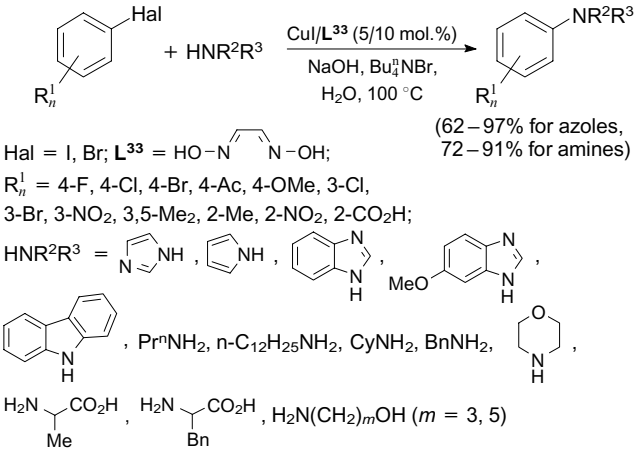
Scheme 63



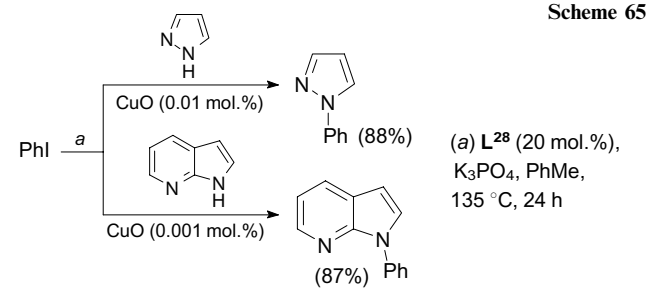
Fu and co-workers [181] used glyoxal (1*E*,2*E*)-dioxime (**L**[33]) to arylate azoles and aliphatic amines in water. In the case of aryl iodides and activated aryl bromides, high product yields were attained (Scheme 64).

By increasing the temperature to 135 °C, Bolm and co-workers [182] made possible the reaction for so-called 'active' azoles at a very low concentration of CuO (0.01 or even 0.001 mol.%) in the presence of 20 mol.% dimethylethylenediamine **L**[28] (Scheme 65).

Scheme 64

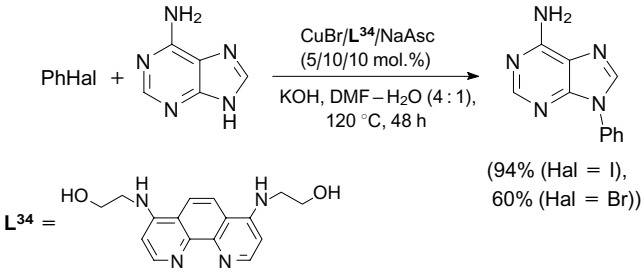


Scheme 65



The arylation of purine bases, for example adenine,[183] in the presence of 4,7-di(2-hydroxyethylamino)-1,10-phenanthroline (**L**[34]) as a ligand and sodium ascorbate was reported (Scheme 66).

Scheme 66



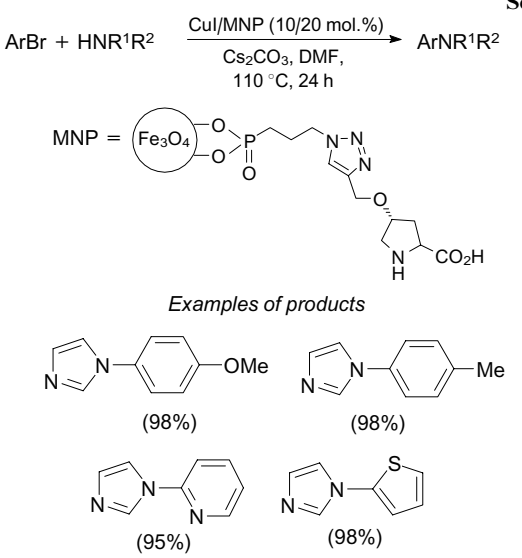
The scope of this review does not allow for detailed consideration of examples of using other metals as aryl halide amination catalysts. Nevertheless, successful use of nickel complexes for this purpose deserves attention.[184, 185] For example, Ni^0 complexes efficiently catalyzed the amination of (hetero)aryl chlorides.[186] The search for optimal catalysts based on Ni^{II} provided the possibility of using aryl- and heteroaryl triflates in these reactions,[187] while Ni^0 immobilized on a magnetic support efficiently catalyzed the amination of aryl sulfamates and carbonates.[188] The complex of nickel bromide with dimethoxyethane in the presence of the $Ru(2,2'\text{-Bpy})_3(PF_6)_2$ photocatalyst (Bpy is bipyridine) was used for continuous flow amination of aryl bromides,[189] while Ru^{II} as a complex with *p*-cymene served as a catalyst for the amination of aryl fluorides.[190] The catalytic synthesis of *N*-aryl- and *N*-hetarylsulfonamides develops along a similar path. The application of $NiBr_2$ in the presence of an Ir^{III} photocatalyst for this purpose [191] and the use of Au^{I} and Au^{III} complexes in the presence of AgOTf for amination, amidation and sulfoamidation of aryl iodides [192] were reported. Special mention should be made of the application of iron-based catalysts for generation of the carbon – nitrogen bond; this issue is extensively reflected in the literature (see, for example, Ref. 193).

3.5. Heterogeneous catalysts in the copper-catalyzed amination

In recent years, extensive studies were carried out on the reactions of amines and azoles with aryl halides catalyzed by copper(I) supported on a variety of materials such as metal oxides, polymers, magnetic materials and various porous materials. Primary attention was given to the supports incorporating magnetic nanoparticles because of easy separation of the catalyst from the reaction mixture. The authors of many studies obtained amination products in high yields both from aryl iodides and from aryl bromides; even aryl chlorides reacted in some cases to give moderate yields of products. The catalyst was reused several times without a noticeable loss of activity. The application of copper and copper oxide nanoparticles in the reactions of amines with aryl halides and with arylboronic acids was considered in detail in a review of Varma and co-workers.[194] Among early publications, mention should be made of the study of Alper and co-workers,[195] who described the synthesis of an oxyproline ligand immobilized on Fe_3O_4 magnetic nanoparticles (MNPs) *via* triazolylphosphonate linker. The reaction of NH-heterocycles with (hetero)aryl bromides was carried out in the presence of 10 mol.% CuI and 20 mol.% MNPs in DMF at 110 °C for 24 h. The yields of the imidazole arylation products exceeded 90% (Scheme 67). Upon recycling of the catalyst, the product yield in the fourth cycle decreased from 98 to 93% (for *p*-methoxybromobenzene).

Copper(I) iodide immobilized in a polymer matrix (10 mol.%) catalyzed reactions of aryl bromides with azoles in the presence of L-proline and potassium carbonate. The reactions carried out in DMSO at 120 °C for 60 h gave products in 97 and 93% yields from *p*-methoxybromobenzene and imidazole and from bromobenzene and benzimidazole, respectively.[196] Aryl chlorides reacted only when

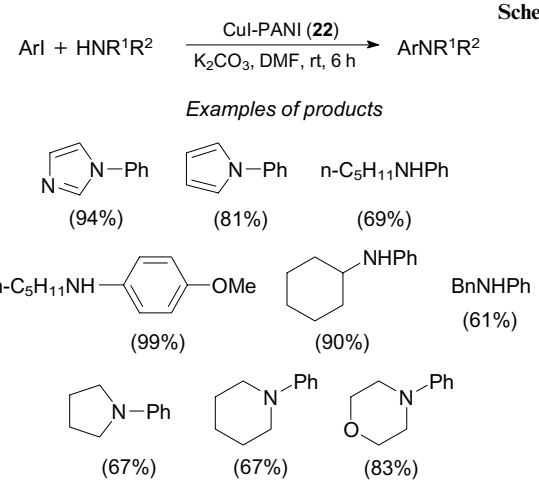
Scheme 67



electron-withdrawing substituents were present in the aromatic ring. This catalyst retained the activity for at least nine cycles.

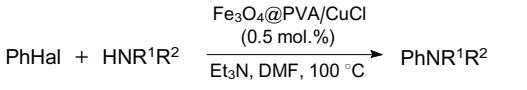
A remarkable result was shown by catalyst **22** supported on polyaniline (PANI):[197] reactions of NH-heterocycles and primary and cyclic secondary amines proceeded at room temperature when 5 mol.% of this catalyst was used under optimized conditions (Scheme 68). Moreover, catalyst **22** was reused almost without the loss of activity: in the reaction of iodobenzene with imidazole, the product yield was 99% in the first cycle and 98% in the fifth cycle.

Scheme 68



As one more example of an efficiently operating catalyst containing magnetic particles, consider the Fe_3O_4@PVA/CuCl system reported by Hekmati and co-workers,[198] in which the Cu^I salt was grafted to a magnetic nanoparticle *via* polyvinyl alcohol (Scheme 69). In the model reaction of iodobenzene with morpholine, this catalyst was recycled eight times, showing a relatively small decrease in the activity.

Scheme 69



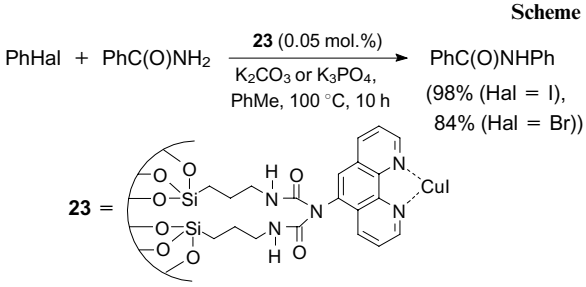
Amine	Yield (%)		
	Hal = I	Hal = Br	Hal = Cl
Morpholine	96	95	60
Piperidine	92		55
Indole	92	90	60
Imidazole	85	80	0

Heterogenized Cu^I complexes were studied in the reactions of NH-heterocycles and amides by Tajbakhsh and co-workers,[199] who used silica gel-supported phenanthroline copper complex **23** (Scheme 70).

Indole reacted with aryl halides also to give product in a high yield (80%) and the catalyst was reused ten times, while the yield gradually and slightly declined.

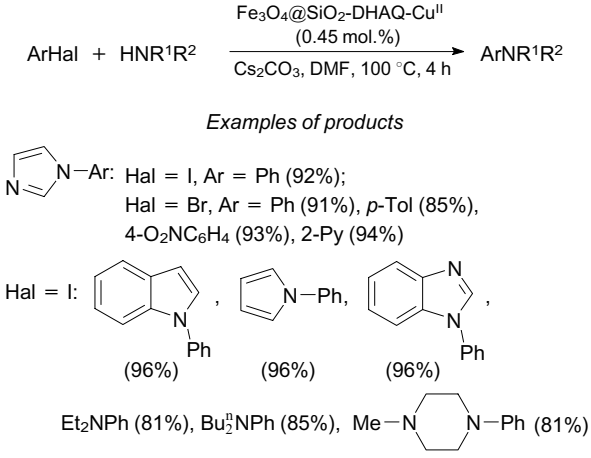
Attention is deserved by a study[200] in which a Cu^{II} complex grafted to a magnetic support *via* 1,4-dihydroxy-9,10-anthraquinone (DHAQ) — Fe_3O_4@SiO_2-DHAQ-Cu^{II} —

Scheme 70



was used as the catalyst for arylation of NH-heterocycles and secondary amines. All products were formed in high yields under relatively mild conditions (Scheme 71). In the case of aryl bromides, the yields were similar to those obtained with aryl iodides; imidazole reacted with chlorobenzene for 24 h to give the product in 43% yield, while in the reaction with *p*-chloronitrobenzene, the yield was 91%. Secondary amines also successfully reacted. The catalyst was recycled six times without a noticeable loss of activity.

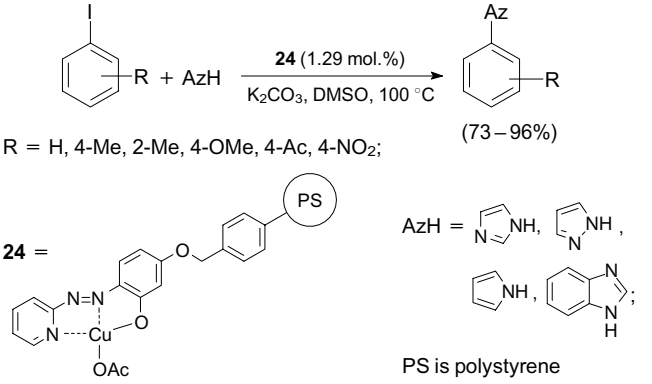
Scheme 71



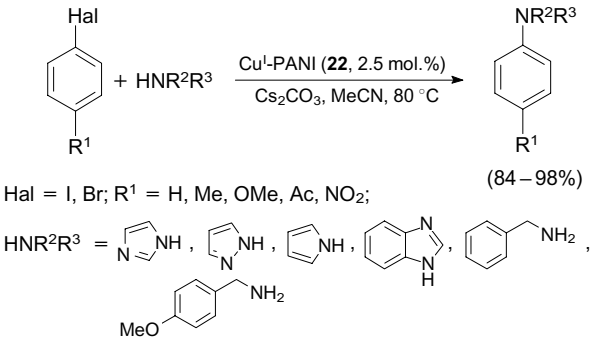
Catalyst **24** based on polymer-supported Cu^{II} successfully catalyzed the Ullmann reaction with aryl iodides (the reaction was much less efficient with aryl bromides); in terms of reactivity, the NH-heterocycles could be arranged in the following order: imidazole > benzimidazole > pyrazole > pyrrole (Scheme 72); the catalyst could be recycled several times without a considerable decrease in the product yield.[201] The reaction of imidazole with aryl iodides provided yields of about 95% (for different substituents in the *para*-position of the benzene ring), and the reaction of aniline resulted in 93% yield. Catalyst **24** was successfully recycled and showed a slight decrease in the yield by the fifth run.

A polyaniline-supported Cu^I catalyst was active not only in the Ullmann arylation, but also in the Chan – Lam reaction and the aza-Michael reaction,[202] which is usually catalyzed by Cu^{II} compounds. As usual, the conditions were optimized in relation to the reaction of iodobenzene with imidazole (Scheme 73), and a high yield of the product was attained (92%). The same yield was obtained in the arylation of pyrazole, while somewhat lower yields were observed in the case of benzimidazole (84%) and pyrrole (88%). The reaction of bromobenzene with imidazole also resulted in a

Scheme 72



Scheme 73



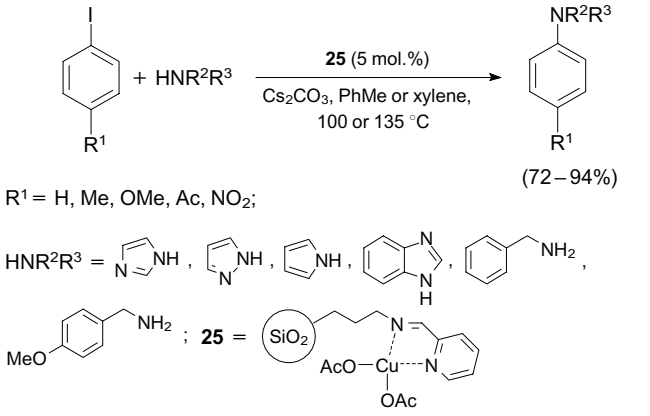
high product yield (90%). The catalyst activity did not decrease over five catalytic cycles.

The immobilized PS-Cu-(2-FuCHO) catalyst was obtained by the reaction of copper(II) acetate with a polystyrene derivative containing Schiff base derived from aniline and furfural. This catalyst was tested in the C – O, C – S and C – N bond formation reactions. The amination was accomplished both as the Chan – Lam reaction involving imidazole and a number of arylboronic acids and as the reaction of iodo- and bromoarenes with imidazole, anilines and benzylamine. The best product yields exceeding 95% were attained for iodobenzene and its derivatives with electron-withdrawing substituents in the *para*-position.[203] It is noteworthy that Cu^{II} complexes immobilized on functionalized epoxy resins showed low efficieny even in the reactions of iodobenzene with imidazole, but were used with high success in the reactions of arylboronic acids.[204]

Silica gel-supported copper complexes proved to be a good choice for Ullmann type reactions. Back in 2007, it was shown [205] that $Cu(OAc)_2$ efficiently catalyzed the reaction of iodobenzene with imidazole (5 mol.% catalyst **25**, Cs_2CO_3, PhMe, 100 °C, 8 h); and aryl bromides without electron-donating groups reacted in a similar way. Imidazole, benzimidazole, pyrazole and pyrrole were also employed as the amine components; even in the case of benzylamine, the product yield was 72%. It was found that the catalyst can be recycled and reused several times. However, in the case of dibenzylamine, the arylation did not take place (Scheme 74).

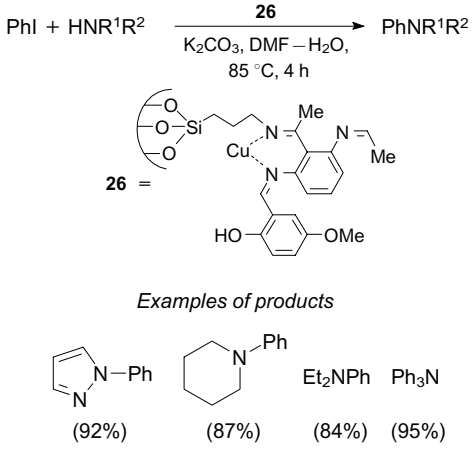
Recently, it was shown [206] that silica gel-supported copper complex with Schiff base smoothly catalyzes the arylation reaction under optimized conditions not only for azoles (pyrazole, benzimidazole, carbazole), but also for secondary amines: for example, 87% yield of the product

Scheme 74



was obtained for piperidine, and 84 and 95% yields were obtained for diethylamine and diphenylamine, respectively (Scheme 75). Catalyst **26** was recycled and reused seven times with a slight decrease in the yield.

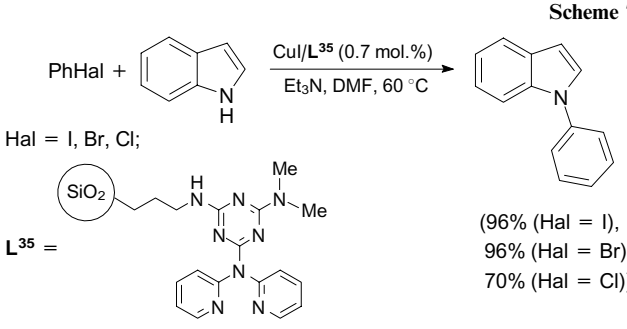
Scheme 75



A heterogeneous catalyst, CuI on SBA-15-immobilized melamine – pyridine (**L**[35]), proved to be efficient and recyclable;[207] the reactions proceeded for not only iodo- and bromobenzene, but also chlorobenzene (Scheme 76). Among amines, benzylamine also reacted with a high yield. Eight runs, accompanied by a minor and smooth decrease in the product yield, were carried out. The authors proposed a catalytic cycle involving Cu^{III}.

Heterogenized CuI supported on thiosemicarbazide-modified carbon nanotubes also showed high activity

Scheme 76

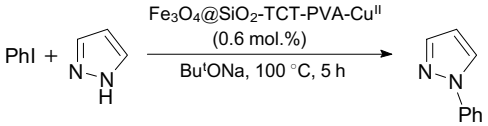


towards reactions of aryl halides (including chlorobenzene) with NH-heterocycles (indole, pyrazole, imidazole) and aniline.[208] The yields of indole arylation products were: 96% for iodobenzene, 92% for bromobenzene and 75% for chlorobenzene. The authors reported the successful use of the catalyst in five cycles.

The magnetic support coated by SiO_2 with a grafted Schiff base coordinating $Cu(OAc)_2$ (22–30 nm size nanoparticles) catalyzed the reaction of iodobenzene with imidazole in DMF in the presence of potassium carbonate base at 120 °C. The reaction product was formed in 82% yield. In the case of bromobenzene, the yield was somewhat lower (75%). Whereas imidazole did not react with chlorobenzene, in the case of 1,4-dichlorobenzene, the arylation did take place.[209] The catalyst stability was insufficient, because the product yield decreased by the fifth cycle to 75%.

However, the copper catalyst Fe_3O_4@SiO_2-TCT-PVA-Cu^{II} (with a particle size of 12–45 nm) incorporated in a polyvinyl alcohol-based magnetic material was well recyclable: a slight decrease in the yield of the product was observed only by the seventh cycle. High yields of the products of arylation with iodobenzene were obtained for imidazole, indole, benzimidazole and pyrrole; arylation was also efficient for 2-iodopyridine.[210] In the case of *N*-phenylpiperazine, benzylamine and di-n-butylamine, the yields somewhat decreased (Scheme 77).

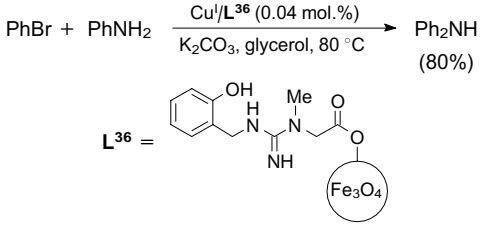
Scheme 77



TCT is (3-chloropropyl)trimethoxysilane,
PVA is polyvinyl alcohol

A reaction catalyzed by the copper complex with Fe_3O_4-grafted guanidine derivative **L**[36] was recently described.[211] The arylation of aniline with bromobenzene in glycerol (0.04 mol.% catalyst, potassium carbonate, 80 °C) resulted in 80% yield; by the fifth cycle the yield of diphenylamine decreased down to 70% (Scheme 78).

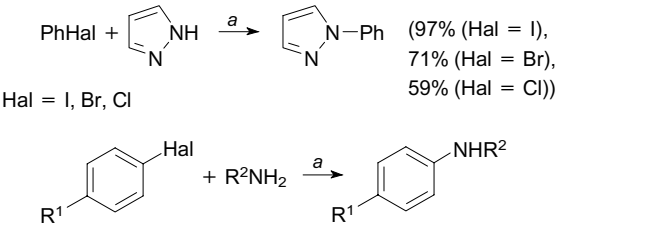
Scheme 78



Ascorbic acid-coated magnetic support containing CuCl proved to be a good catalyst for the arylation of not only NH-heterocycles, but also aromatic and aliphatic amines.[212] The reaction proceeded in water at room temperature in the presence of KOH as the base (Scheme 79). Aniline, benzylamine and n-butylamine reacted equally efficiently under these conditions. The catalyst can be recycled and reused up to six times without decrease in the efficiency.

Triazine-based dendrimer system **27**, immobilized on silica incorporating a magnetic filler, served as a support for copper nanoparticles (Cu-NPs).[213] Due to complication of the catalyst structure, it was necessary to increase the

Scheme 79

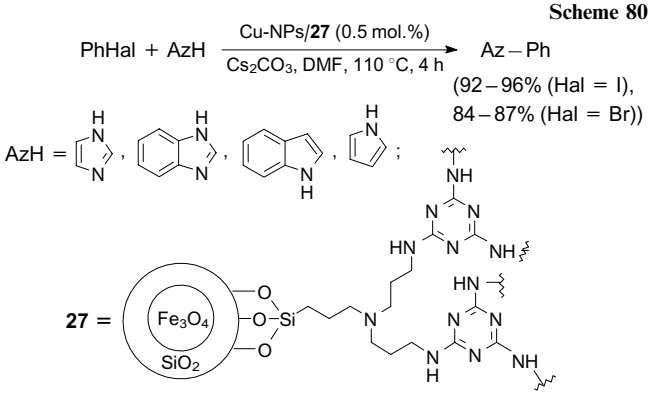


a — Cu/AscH@MNPs, KOH, H_2O, rt, 6 h;
MNPs are magnetic nanoparticles;
Hal = I, Br, Cl; R^1 = H, NO_2; R^2 = Ph, Bn, Bu^n

R^1	R^2	Hal	Yield (%)
H	Ph	I	96
H	Ph	Br	52
NO_2	Ph	Cl	61
H	Bn	I	97
H	Bn	Br	87
H	Bn	Cl	67
NO_2	Bn	Cl	51
H	Bu^n	I	92
H	Bu^n	Br	90

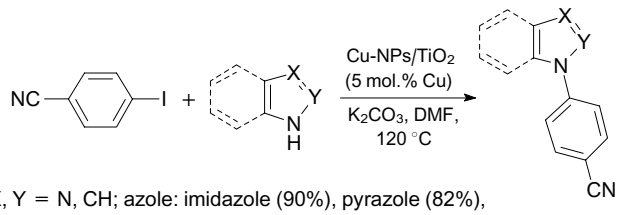
reaction temperature to 110 °C [Scheme 80; wave lines correspond to the dendrimer branching sites: tris(3-aminopropyl) groups 'grow' from triazine positions 4 and 6, while on their amino groups, next-generation triazine molecules are located, *etc.*]. NH-Heterocycles such as imidazole, benzimidazole, indole and pyrrole were successfully arylated with iodobenzene; reactions with bromobenzene and with *N*-phenylpiperazine were also studied.

Scheme 80

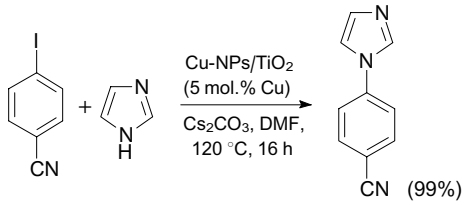


Copper nanoparticles were supported on various solid materials to carry out amination reactions.[214] In the presence of the resulting catalysts, amination of *p*-iodobenzonitrile with various azoles — imidazole, pyrazole, benzimidazole and indole — was carried out (Scheme 81). Among the materials tested as supports (carbon, zeolites, montmorillonite K10, *etc.*), TiO_2 proved to be the material of choice: the yields of amination products ranged from 59 to 90%. When K_2CO_3 was replaced by Cs_2CO_3, the yields were, in some cases, almost quantitative. It is noteworthy that in the presence of these catalysts, the yields of products were retained in 3–4 successive cycles.

Scheme 81



X, Y = N, CH; azole: imidazole (90%), pyrazole (82%), benzimidazole (72%), indole (59%)

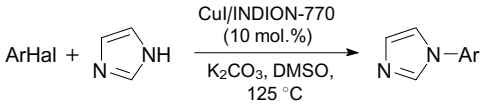


Copper(I) iodide in combination with sulfonic acid-containing cation exchange resin INDION-770, which is commercially available, catalyzed the reaction of aryl halides with imidazole (Scheme 82).[215] The reactions with aryl iodides and bromides proceeded smoothly, while in the case of aryl chlorides, only *p*-nitrochlorobenzene reacted. The recyclability of this catalyst was moderate: from the third cycle, the product yields started to decrease.

We will briefly mention other ways of immobilization of Cu catalysts, in particular, on polystyrene-based materials. Thus copper(II)-containing polymer with alanine moieties for the coordination of copper cations was used for amidation of aryl halides without a solvent; the authors demonstrated the possibility of conducting this reaction for a broad range of substrates.[216] In 2017, a review on the use of polystyrene-supported copper complexes, in particular, for the C – N bond formation was published.[217]

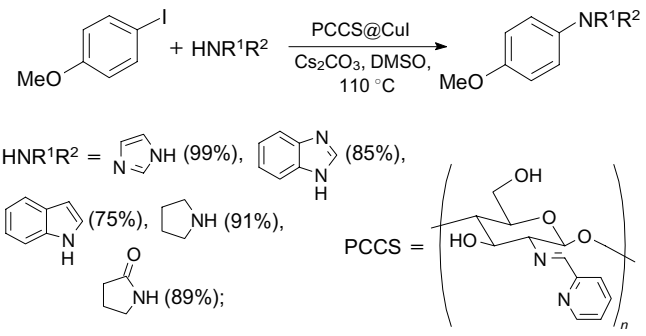
Other polymers were also proposed for immobilization of copper catalysts. For example, CuI complex with modified chitosan (PCCS) proved to be an efficient catalyst for the arylation of amines, amides and azoles.[218] Primary and secondary amines successfully reacted with aryl iodides and bromides (aryl chlorides did not react under these conditions) in the presence of Cs_2CO_3 in DMSO at 100 °C to give the desired products in up to 99% yields (Scheme 83). The catalyst withstood five cycles without the loss of activity.

Scheme 82



Ar = Ph (94% (Hal = I), 89% (Hal = Br)), 4-$MeOC_6H_4$ (91% (Hal = Br)), 4-$O_2NC_6H_4$ (94% (Hal = Cl))

Scheme 83



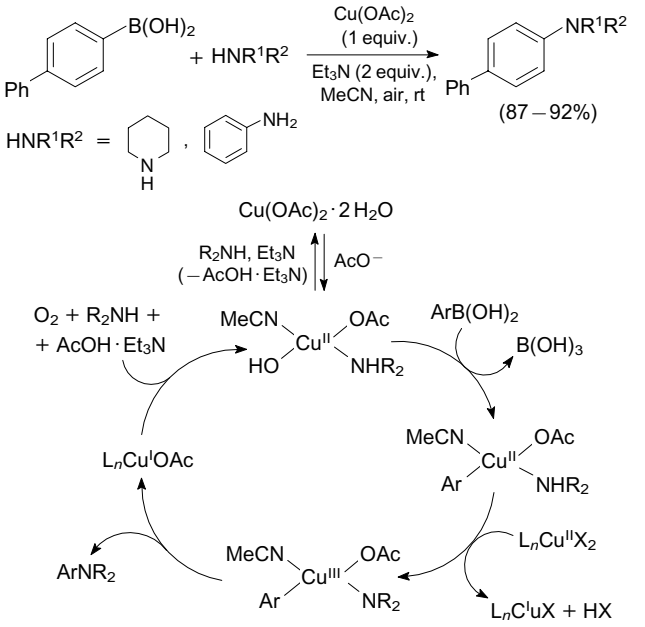
4. Chan – Lam reaction (copper-catalyzed amination of arylboronic acids)

The methods of C(sp^2) – N bond formation by the Buchwald – Hartwig reaction and by the catalytic Ullmann – Goldberg reaction considered above opened up new synthetic opportunities for the preparation of various classes of nitrogen-containing compounds. However, both methods have shortcomings. The Buchwald – Hartwig reactions require the use of expensive palladium and rather costly ligands. In addition, the reactions are often accompanied by the formation of minor products resulting from hydrodehalogenation, which is rather difficult to avoid, since the pathways to the major and minor products are similar. The catalytic Ullmann reaction, although implies much less expensive catalytic systems, is inferior to palladium-catalyzed reactions in the synthetic scope. This is why the alternative pathway to C(sp^2) – N bond formation proposed independently by research groups headed by Chan[219] and Lam[220] and based on the Cu^{II}-catalyzed reaction of amines with arylboronic acids is an important achievement of modern chemistry.

Unlike the two methods considered above, which are based on the catalytic reaction between nucleophilic and electrophilic reagents, in this case, both reagents are nucleophiles. The reaction uses available copper acetate, weak bases and cheap solvents; it proceeds at room temperature and does not require inert atmosphere or external ligands.[221] As a historical note, it should be borne in mind that the Chan – Lam reaction, like other types of cross-coupling, has made a certain path, during which various organoelement compounds were investigated. These studies were initiated by Russian scientists, V.A.Dodonov and A.V.Gushchin,[222] who used triphenylbismuth diacetate for the arylation of amines in the presence of copper. A similar transformation was later described by Barton *et al.*[223] and Chan.[224] However, non-toxic boronic acids proved to be most demanded, as in the case of C(sp^2) – C(sp^2) cross-coupling reactions. It is also noteworthy that in 1998, reaction of this type between arylboronic acids and phenols was accomplished by West and co-workers,[225] who thus proposed an alternative method for the formation of the C(sp^2) – O bond.

Owing to its simplicity, the Chan – Lam approach found wide use in organic synthesis.[226] Conditions for efficient preparation of compounds with various C(sp^2) – Nu bonds in the presence of catalytic amounts of copper complexes were elucidated owing to the efforts of many research groups.[227, 228] The benefits of this method include the use of available Cu^{II} salts and no need for additional ligands or strong bases. Despite the seeming simplicity of the reaction (Scheme 84), its mechanism is still a debated issue, and the formation of copper(III) *via* disproportionation of the intermediate organic copper salt, proposed by Stahl and co-workers,[229] as well as Cu^{II} disproportionation and reductive elimination lack strong evidence. The complexity of this process is demonstrated by the detailed investigation of the mechanism of model reaction of $ArB(OH)_2$ (Ar = 4-PhC_6H_4) with two amines (aniline and piperidine) in the presence of a stoichiometric amount of copper, reported by Watson and co-workers.[230] Scheme 84 shows the catalytic cycle proposed by the authors.

Scheme 84



It can be seen from this cycle that the nature of the amine can have a considerable influence on the course of the reaction. Thus, the simplicity of this reaction bumped up against the complexity of studying and understanding of mechanism and pronounced dependence of the reaction outcome on the type of reactants, the nature and concentration of the copper catalyst and also on the natures of oxidant, solvent, base and additives, the presence of water and even temperature. A great contribution to investigation of the reaction mechanism was made by Schaper's research group, who carried out thorough kinetic experiments and proposed catalytic cycles involving sulfonato-diketimine [231] and iminoarylsulfonate [232] copper(II) complexes.

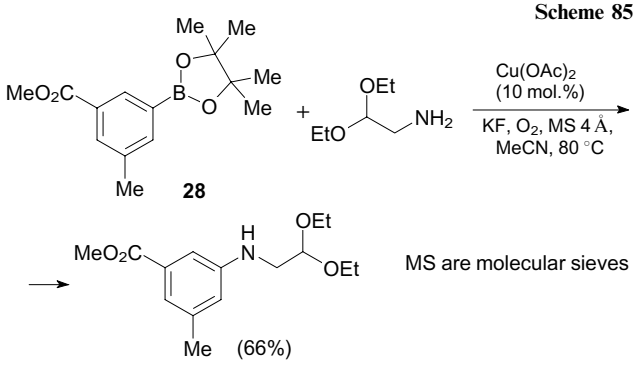
4.1. Homogeneous conditions

There are quite a few procedures the successful use of which depends on the nature of reactants.[230 – 235] This is clearly illustrated by the fact that the readily proceeding reaction of amines with $ArB(OH)_2$ is not always efficient when involves pinacol esters of boronic acids, although such transformations are still known. For example, Hartwig and co-workers [236] performed the amination of arylboronic acid pinacol ester **28** with various primary amines in the presence of KF (Scheme 85).

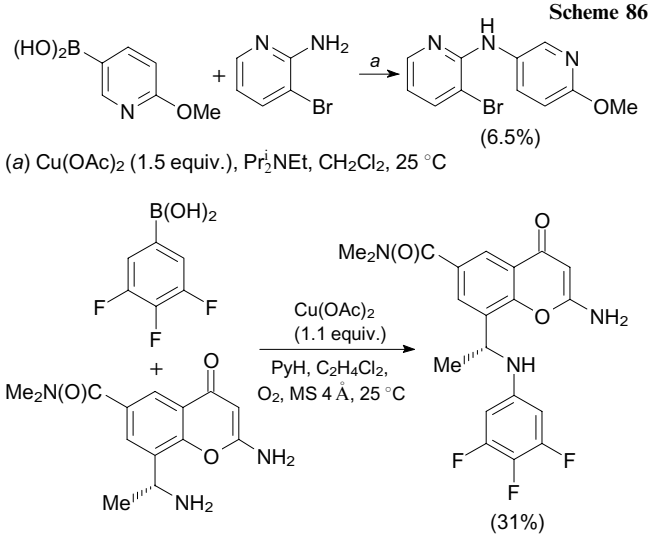
Reactions of this type were carried out using not only arylboronic acids, but also boroxines, boric acid esters and trifluoroborates, although their use is still limited to few examples. In addition to arylboronic acids, in the presence of stoichiometric amounts of copper acetate, alkylboronic acids can also react. The nature of the ligand is also important for this reaction and can affect the mechanism; numerous possible reaction pathways were reported in the literature. However, in most studies, if a poorly soluble copper salt is not used as the precursor, the reaction is carried out without a ligand, because copper acetate is readily soluble in organic solvents. Back in their early study in 1998, Lam and co-workers [220] established the following order of efficiency of solvents for the arylation of imidazole: CH_2Cl_2 > 1,4-dioxane > *N*-methylpyrrolidone ~ THF ~ DMF ≫ ethyl acetate ≈ toluene ≈ DMSO. Optimization of the conditions for a particular reaction requires selection of a particular base, accelerating additive and oxidant. Most often, the presence of oxygen, which oxidizes Cu^{I} to Cu^{II}, is sufficient for the reaction to occur. However, the use of more potent oxidants such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or pyridine *N*-oxide may lead to oxidation of Cu^{II} to Cu^{III}. All these aspects are still being addressed. An interesting idea is to apply photocatalysis to the Chan – Lam reaction, which would markedly facilitate the conversion of Cu^{II} to Cu^{III}.

As noted above, this approach was used to arylate (hetero)arylamines, -amides, -sulfonamides and various NH-heterocycles. Due to high demand for the products of these reactions, aromatic amines have been studied most widely. Quite a few pharmaceuticals have been obtained from these substrates, *e.g.*, a succinate-cytochrome C-reductase inhibitor,[237] retinoic acid 4-hydroxylase (CYP26) inhibitors,[238] β3-adrenergic receptor agonists,[239] MEK kinase inhibitors [240] and selective agonists of formyl peptide receptors (FPR).[241] The yields of products were sometimes relatively low,[242, 243] the reactions were often conducted as non-catalyzed versions; most likely, the authors did not aim to optimize the procedures they used. Examples of these reactions are depicted in Scheme 86.

Scheme 85



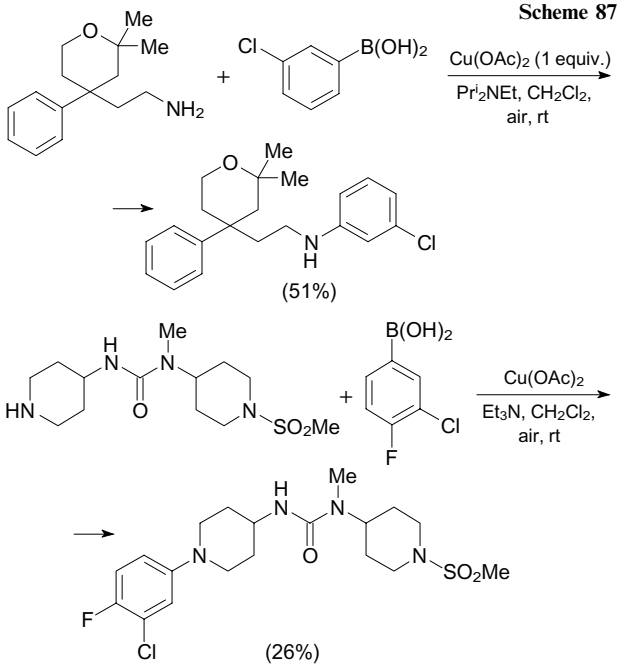
Scheme 86



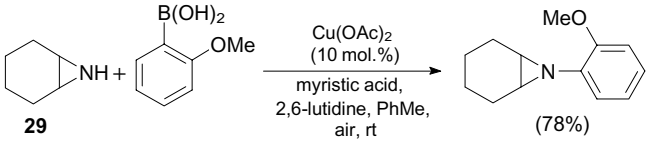
Primary and secondary cyclic alkylamines showed good results in the Chan – Lam amination and are already widely used to prepare potential drugs, for example, inhibitor of isoprenylcysteine carboxyl methyltransferase [244] or ureido NPY Y5 receptor antagonists.[245] (Scheme 87).

Bicyclic aziridine derivative **29** was also successfully used in this reaction (Scheme 88).[246]

Scheme 87

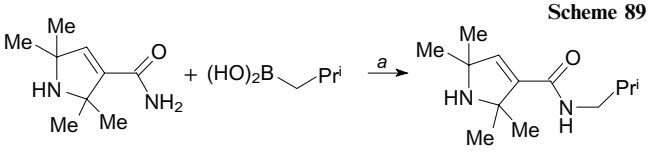


Scheme 88

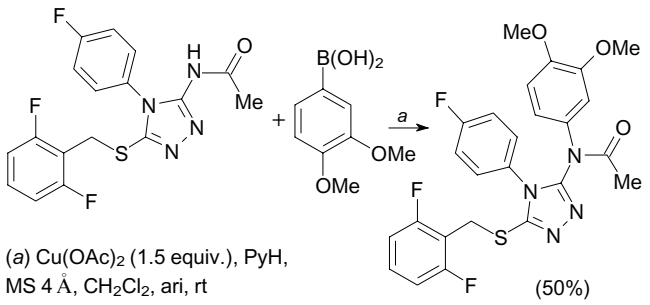


The reactions with primary and secondary amides were carried out (the products of the latter are of interest for pharmaceutical production) using not only aryl-, but also alkylboronic acids (Scheme 89).[247, 248]

Scheme 89



(*a*) CuBr (10 mol.%), NaOTMS, $(Bu^tO)_2$, Bu^tOH, 75 °C

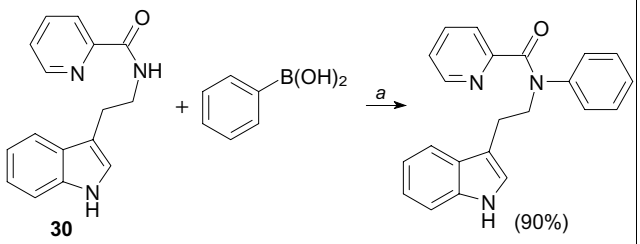


(*a*) $Cu(OAc)_2$ (1.5 equiv.), PyH, MS 4 Å, CH_2Cl_2, ari, rt

When a chelating system is present in the starting molecule (compound **30**), the arylation of the amide nitrogen atom with phenylboronic acid occurs with a high yield of product (Scheme 90).[249]

Obviously, the use of the Chan – Lam reaction for the arylation of NH-heterocycles, especially for the preparation of biologically active compounds, holds great promise. The

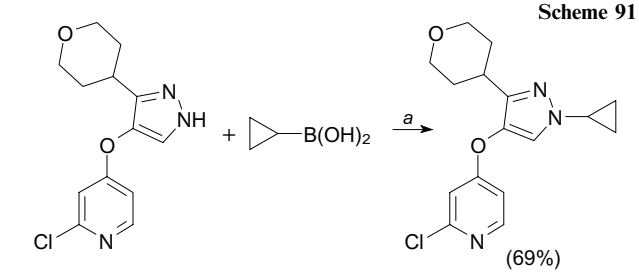
Scheme 90



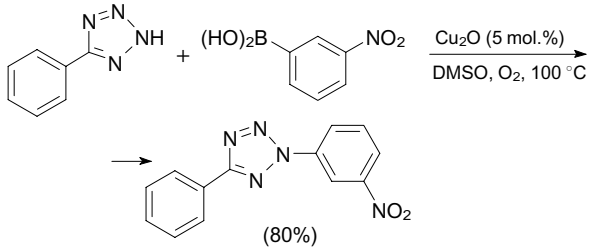
(*a*) $Cu(OAc)_2 \cdot H_2O$ (20 mol.%), DMAP (20 mol.%), KI (20 mol.%), DMF, air, rt

substrates successfully used for this purpose include pyrrole, imidazole,[250] pyrazole,[251] tetrazole,[252] indole [253] and pyrazinone;[254] note that the reaction conditions are substantially different, depending on the structure of the heterocyclic compound when aryl- or alkylboronic acids are used (Scheme 91).

Scheme 91

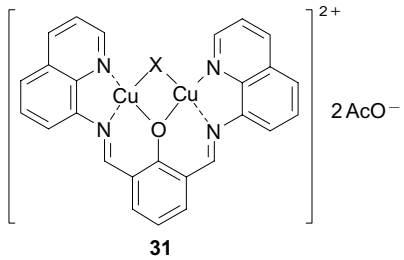


(*a*) $Cu(OAc)_2$ (12.5 mol.%), 2,2′-Bpy (18.85 mol.%), valeric acid (25 mol.%), Pr^iNEt_2, THF – DMSO (1 : 1), 5% O_2/N_2, 90 °C



Recently, it was shown that N-arylation of 3,4,5-trisubstituted pyrazoles can be carried out at room temperature;[255] broad prospects are opened by vinylation of 1,2,3-triazoles and tetrazoles into position 2 with vinylboronic acid or potassium vinyltrifluoroborate.[256] The search for the most efficient copper complexes for catalysis of the Chan – Lam reaction is in progress: for example, binuclear Cu^{II} complex **31** with bis(quinoline) Schiff base proved to be a good choice for conducting the reaction at room temperature.[257] On the basis of kinetic experiments,

Structure 31



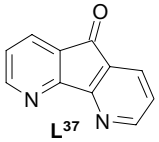
31

the authors proposed a mechanism of the catalytic cycle involving binuclear complex **31**.

Similarly, a high efficiency was found only for the copper complex [Cu**L**[37]](OTf)$_2$ with 4,5-diazafluorenone.[258]

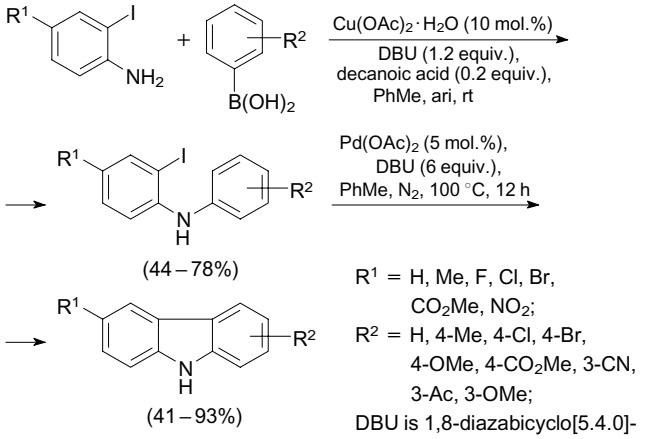
For successful use of low-reactive anilines in the Chan – Lam reactions, Gale-Day and co-workers[259] proposed to activate the reaction by conducting it in an electrochemical cell with copper anode and cathode. This allowed the synthesis of various functionalized diarylamines in high yields under mild conditions.

Structure L[37]



There are interesting synthetic sequences that include the Chan – Lam reaction followed by intramolecular cyclization (C – H activation), giving rise to heterocyclic systems. In the first step, substituted diphenylamines are obtained, while the second step represents Pd^{II}-catalyzed formation of the C – C bond from intermediate *o*-iodo derivatives, thus furnishing a representative series of carbazoles (Scheme 92).[260]

Scheme 92

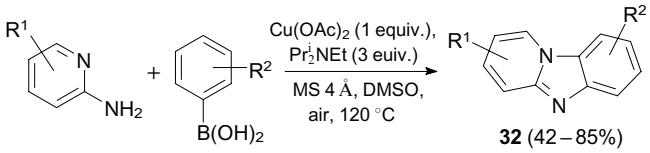


Similarly, benzimidazopyridines were obtained from 2-aminopyridines and arylboronic acids by a one-pot procedure.[261] The reaction was carried out in the presence of a stoichiometric amount of copper acetate in DMSO at 120 °C in air; the yields of heterocyclic products **32** varied from moderate to high, depending on the positions of substituents in the starting compounds (Scheme 93).

Using the Chan – Lam method, it was possible to successfully perform arylation of primary and secondary sulfonamides [262, 263] and sulfoximines.[264] In the case of possible competition between the aniline and sulfonamide nitrogen atoms, divergent regioselectivity can be attained by varying the reaction conditions (Scheme 94).[265]

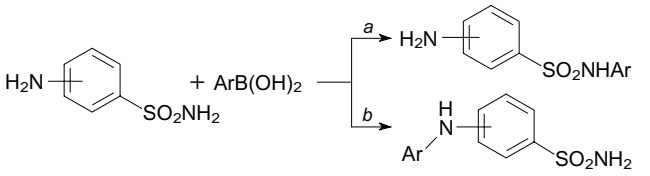
Recently, efficient use of Ni^{II} catalyst in the Chan – Lam reaction was reported.[266] Nickel carbene complex **33** was used in the presence of an additional ligand — 4,4′-dimethyl-2,2′-bipyridine (Me_2Bpy). The reactions with primary and secondary amines were studied; moderate activity of this catalyst in the reactions with amides and pronounced

Scheme 93



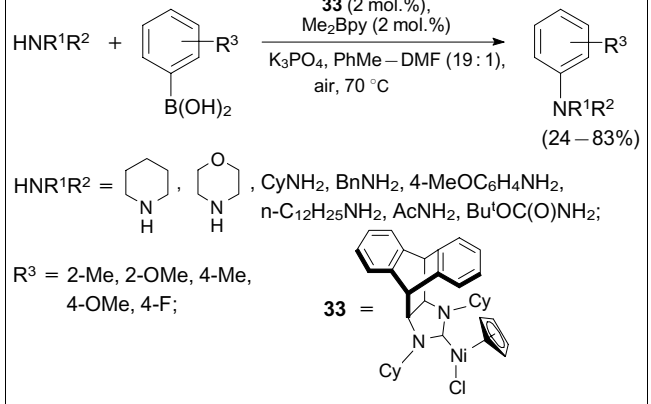
R^1 = H, 4-Me, 3-Me, 3-OBn; R^2 = H, Me, Cl, Br, I, Ac, OMe, CO_2Me, CH_2OH (in different positions), 4-CF_3

Scheme 94



(*a*) CuCl (40 mol.%), Et_3N, dioxane, air, rt;
(*b*) 2-ThC(O)OCu (20 mol.%), 2,6-lutidine, DMF, air, rt

Scheme 95



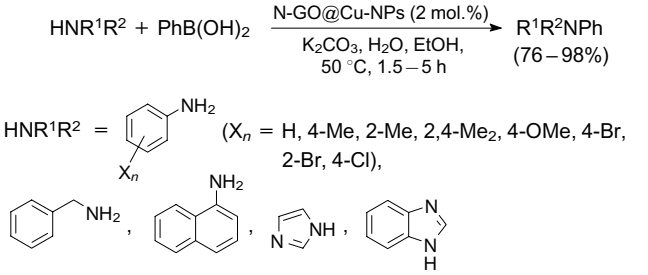
dependence of the product yields on the reactant structure were demonstrated (Scheme 95).

4.2. Application of immobilized catalysts

As in the case of Cu^{I}-catalyzed amination, Chan – Lam reaction procedures using heterogeneous catalysis have been actively developed in recent years. Many of these catalysts, including those mentioned above,[201 – 205] are often employed for both reactions. For example, the arylation of diverse NH-heterocycles with arylboronic acids in methanol was successfully carried out in the presence of polystyrene-supported copper(II) complex.[267] A catalyst based on copper nanoparticles immobilized on N-doped graphene oxide (N-GO) was developed.[268] Reactions of diverse amines with phenylboronic acid made it possible to obtain diarylamines in high yields (except for reactions with 2- and 4-nitroanilines). The recyclability of this catalyst follows from the retention of product yields for up to five reaction cycles (Scheme 96).

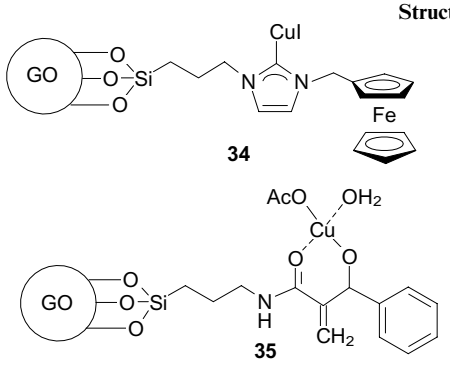
Graphene oxide modified with propylsiloxane derivative bearing a 1-ferrocenylmethylimidazole moiety was used to obtain Cu^{II} complex **34**, which was studied in the reactions of formation of *N*-arylsulfonamides.[269] The catalyst can be used in six successive cycles without loss of activity.

Scheme 96



One more graphene oxide-supported copper(II) complex **35** was utilized to obtain unsymmetrical diarylamines from anilines and boric acids.[270] By varying substituents in both reactants, the authors showed that the reactions of aniline and *p*-toluidine with arylboronic acids containing methyl, methoxy, nitro and cyano groups give target products in 70 to 90% yields. The recyclability of catalyst **35** was confirmed experimentally in four successive catalytic cycles.

Structures 34, 35

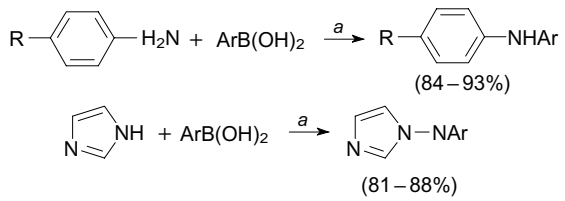


The simplest Cu^{II} complex with a Schiff base was immobilized on graphene oxide using (3-aminopropyl)trialkoxysilane linker; this gave an efficient catalyst for the Chan – Lam reactions, which ensured 70 – 88% yields of unsymmetrical diarylamines.[271] No significant decrease in the catalyst efficiently was observed over five cycles.

Copper(II) oxide nanoparticles with an average size of 7 – 17 nm, obtained by a simple procedure from the corresponding chloride, were used in the reactions of arylboronic acids with a number of anilines and imidazole at room temperature; the yields of products exceeded 80% in all cases (Scheme 97).[272] The possibility of recycling copper oxide nanoparticles was tested, and it was demonstrated that the catalyst activity is retained over the first three cycles.

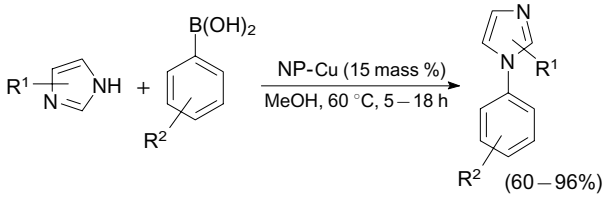
Similarly, spherical CuO nanoparticles (~6 nm average size) proved to be efficient in the arylation of simple

Scheme 97



(*a*) NP-Cu (30 mol.%), K_2CO_3, MeOH – H_2O (1 : 1), rt, 8 – 12 h;
R = H, Br, OMe; Ar = XC_6H_4 (X = H, 4-Et, 4-F, 4-Cl, 4-OMe, 4-Bu^t, 3-Me)

Scheme 98

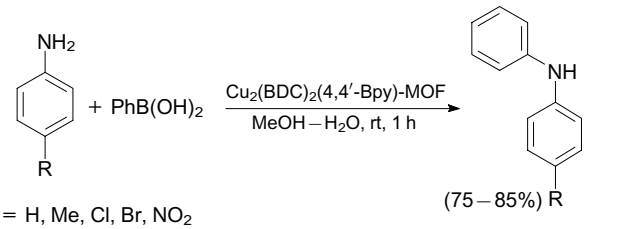


R^1 = H, 2-Me, 4-Me, 5-Me; R^2 = H, 4-F, 4-Cl, 4-OMe, 3-Me

imidazoles (Scheme 98); this reaction did not require addition of a base.[273] The catalyst loading was 20 mg of nanoparticles per mmol of the starting imidazole.

The metal-organic framework (MOF) containing Cu^{II} compounds in the nodes and based on terephthalic acid (BDC) and 4,4′-bipyridine was studied in reactions of some anilines with phenylboronic acid.[274] The yields of arylation products were 75 – 85%; the catalyst was used several times without decrease in the yields of target compounds (Scheme 99).

Scheme 99

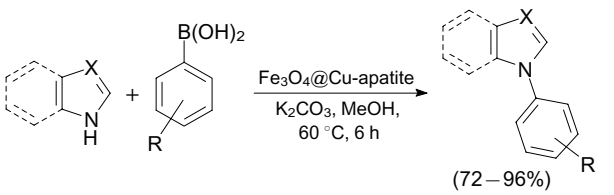


R = H, Me, Cl, Br, NO_2

One more catalyst (URJC-1), a MOF based on 4,5-di(tetrazolyl)-1*H*-imidazole and $Cu(NO_3)_2$, was also tested in reactions of phenylboronic acid with a number of amines.[275] The yields of products were 61 – 84% for arylamines and 41 – 71% for alkylamines. The efficiency of this heterogeneous catalyst did not change significantly over five cycles.

Nanostructured Fe_3O_4 encapsulated into the Cu – apatite composite was studied as a recyclable catalyst of the Chan – Lam reaction.[276] High yields of arylation products were obtained in reactions with imidazole and indole (Scheme 100). The catalyst could be reused five times.

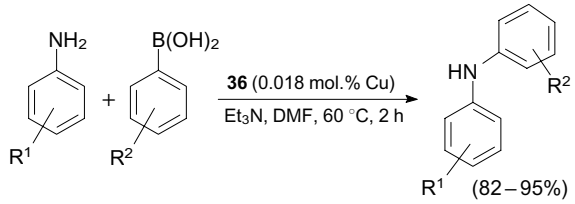
Scheme 100



X = CH, N; R = H, 4-Me, 3-Me, 2-Me, 4-OMe, 4-NO_2

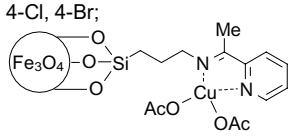
The catalytic properties of Cu^{II} iminopyridyl complex grafted to the magnetic Fe_3O_4 particles *via* 3-aminopropylsiloxane linker (catalyst **36**) were studied in reactions of arylboronic acids with a number of anilines (Scheme 101).[277] The yields of the corresponding diarylamines were 82 – 95%; the possibility of using the catalyst in five cycles with gradual decrease in the activity was demonstrated.

Scheme 101



R^1 = H, 4-Me, 4-OMe, 4-NO_2, 4-Ac;
R^2 = H, 3-Me, 4-Me, 4-Et, 4-Cl, 4-Br;

36 =



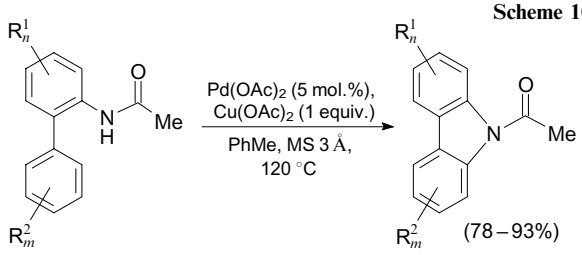
The search for other solid supports for immobilization of the copper catalyst used in the Chan – Lam reactions is in progress. For example, sorption of copper(II) sulfate on montmorillonite K-10 gave a catalyst that allowed for arylation of imidazole derivatives with up to 93% yields; this catalyst could be reused in four successive cycles with a minor decrease in the activity.[278] A bimetallic Pd – Cu catalyst supported on $SiO_2 - TiO_2$ *via* diamine linkers was developed. Using numerous examples, the efficiency of this catalyst in the Chan – Lam and Suzuki reactions and the catalyst reuse for up to five times were demonstrated.[279]

5. Amination using metal-catalyzed CH-activation

The use of simple arenes or heteroarenes instead of aryl halides or arylboronic acids in the cross-coupling reactions to give the C(sp^2) – N bond is evidently a new atom-economical strategy for the synthesis of amino derivatives, resulting in metallation of the activated C – H bond with subsequent oxidation of the carbon atom to give the C – N bond. Quite recently, these reactions seemed difficult to implement, but now they are the subject of extensive literature including reviews.[280 – 289] The successful implementation of these reactions started from the use of arenes containing functional groups (so-called directing groups) capable of being coordinated to a metal and directing its addition to the *ortho*-position. In the case of intramolecular amination, the amino group can perform a dual function being both a reacting and a directing group. These reactions are catalyzed by Pd^{II} in the presence of oxidants (oxygen or Cu^{II}). The metallation of arene gives a metallacycle, and reductive amination affords the product and Pd^0, which is oxidized to Pd^{II}. This oxidative reaction was first carried out in 2005 by Buchwald and co-workers[290] in the synthesis of aza heterocycles, including carbazoles (Scheme 102).[291] Subsequently, indazoles,[292] oxindoles,[293] benzimidazoles,[294] 1-aryl-1*H*-benzotriazoles,[295] quinazolinones[296] and diverse indoles and carbazoles[297] were obtained by this method using various oxidants.

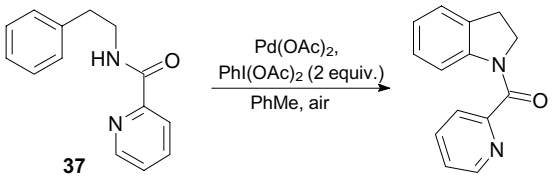
One more type of these reactions that occur even at room temperature includes the use of a strong oxidant able to oxidize Pd^{II} to Pd^{IV} in the metallated arene; after that, Pd^{IV} easily undergoes reductive elimination. An example of such reaction is the synthesis of carbazole in the presence of $PhI(OAc)_2$. In the oxidative reactions, the use of bidentate chelators, *e.g.*, 2-pyridinecarboxylic acid amide **37**, as directing groups, proposed by Nadres and Daugulis[298] and Chen and co-workers,[299] was found to be especially efficient (Scheme 103).

Scheme 102



R^1_n = H, 5-Me, 5-F, 5-CF_3, 3,5-Me_2, 3,5-F_2;
R^2_m = 6-F, 6-OMe, 6-CF_3, 4-OMe, 4,6-$(OMe)_2$

Scheme 103



37

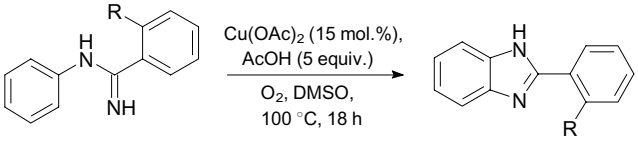
Amount of $Pd(OAc)_2$, mol.%	*T*, °C	Yield (%)
5	100	80
2	60	88

The same principle,[300 – 302] but with replacement of the traditional phenyliodonium acetate as oxidant by more potent phenyliodonium dimethyl malonate, was used to prepare benzazetidine difficult to obtain by other methods.[303, 304] The use of bidentate chelators markedly improved the reaction conditions, namely, this decreased the temperature, amount of the catalyst and the reaction time. The directing group and the substituents in the arene have a considerable influence on the amination.

5.1. Cu^{II} catalysis of C – H-amination

The possibility of using copper salts and complexes as catalysts play an enormous role for the practical application of the C – H amination. The first example of intramolecular amination catalyzed by $Cu(OAc)_2$ in the presence of oxygen was reported by Brasche and Buchwald[305] in the synthesis of benzimidazoles (Scheme 104).

Scheme 104

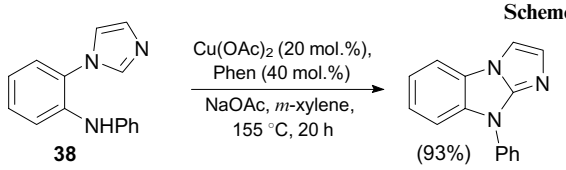


R = H, Me, CF_3 (69 – 89%)

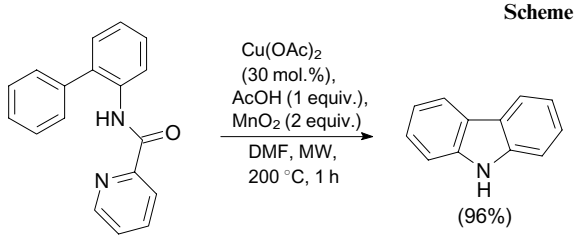
These reactions can be carried out for heterocycles with acidic C – H bond that can be easily metallated, as, for example, in imidazole **38** (Scheme 105).[306]

Miura and co-workers[307, 308] utilized this method to prepare carbazole and indolines using microwave radiation and MnO_2 as the oxidant (Scheme 106). The reaction occured more readily when chelating directing groups were present in the reactant. Not only intramolecular, but also intermolecular reactions of arylation of azoles, primary amines and secondary cyclic amines were carried out in this way.[301] It is beyond doubt that that intermolecular amination is more problematic. These reactions were

Scheme 105



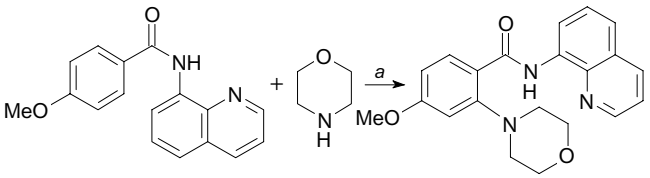
Scheme 106



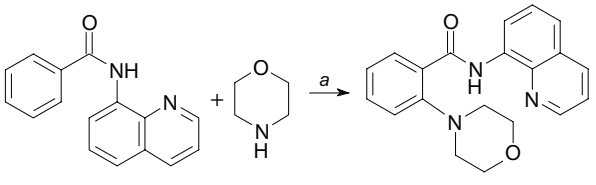
accomplished using not only palladium and copper, but other metal catalysts, such as Co, Ni, Rh, Ru, Au, although with only a narrow range of substrates, usually amides or electrophilic aminating agents.

The use of 8-aminoquinoline moiety as the directing group was a lucky idea for intermolecular type reactions. Examples of using this moiety in the reaction with morpholine catalyzed by Cu^{II} in the presence of 4-morpholine *N*-oxide (NMO) and Ag_2CO_3 oxidants or catalyzed by Ni^{II} in the presence of Ag_2CO_3 oxidant are shown in Scheme 107.[309]

Scheme 107



(*a*) $Cu(OAc)_2$ (10 mol.%), Ag_2CO_3 (13 mol.%), NMO (2 equiv.), NMP, 110 °C



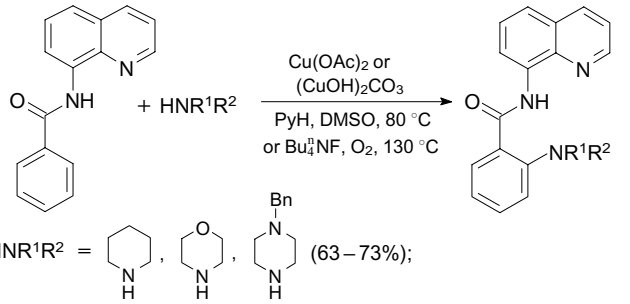
(*a*) $Ni(OAc)_2$, Ag_2CO_3, Na_2CO_3, PhMe, 140 °C, 10 h

Later Daugulis's research team[302] used the 8-aminoquinoline moiety as the directing group and oxygen as the oxidant to carry out Cu-catalyzed arylation and heteroarylation of various amines, including primary aliphatic amines, azoles and sulfonamides (Scheme 108).

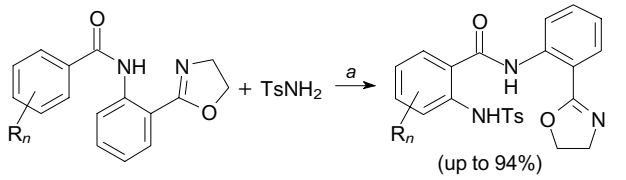
The same directing group was used in the $Cu(OAc)_2$-catalyzed amidation with sulfoximines.[310] One more bidentate directing group was involved in the Cu^{II}-catalyzed amidation of aryl- and heteroarylamides reported by Yu and co-workers [311] (Scheme 109).

A variation of substituents in the arene or the nature of the directing group strongly affects the outcome of amination,[312, 313] and with a good combination, this reaction can proceed even at room temperature.[314] Miura and co-workers [315] showed that the copper-catalyzed reaction of enamide may give substituted indole or the product of alkoxylation of the vinyl group — 2,4,5-trisubstituted oxazole, depending on the nature of substituents in the directing group. In other words, the directing group controls the cyclization (Scheme 110).

Scheme 108

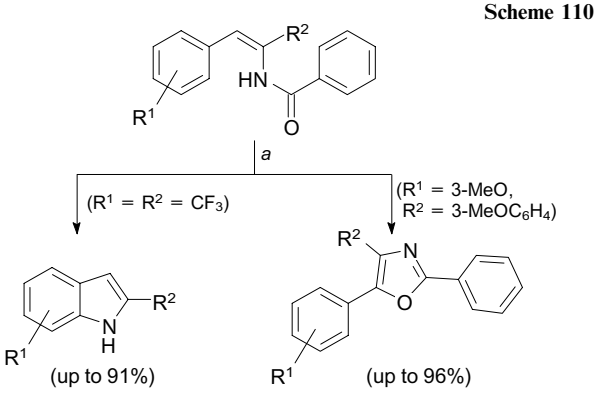


Scheme 109



(*a*) $Cu(OAc)_2$ (1 equiv.), Na_2CO_3, DMSO, air, 80 °C;
R_n = 2-Me, 4-Me, 2,4-Me_2, 3-OMe, 4-OMe, 4-Ph, 2-F, 3-F, 4-F, 3-Cl, 4-Cl, 4-Br, 2-CF_3, 3-CF_3, 4-CF_3

Scheme 110



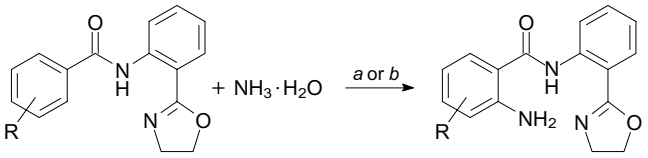
(*a*) $Cu(Bu^tCO_2)_2$ (30 mol.%), MnO_2, Bu^tCO_2H, DMF, MW, 200 °C, 1 h

It is noteworthy that the young field of chemical science related to C – H-activation, especially combined with the intermolecular amination, is being developed very rapidly. The first reactions using a stoichiometric amount of $Cu(OAc)_2$ and 2-pyridyl directing group were reported in 2006,[316, 317] and as soon as in 2010, Li and co-workers [318] performed these transformations in the catalyzed version, although using a strong oxidant ($CuBr - Bu^tOOBu^t$ system) and high temperature (120 °C).

Nevertheless, in complicated cases, for example, when ammonia is used as the aminating agent, it is not always possible to successfully use particularly catalytic amounts of copper(II) in the reaction, even when the original activating group has been thoroughly chosen.[319] As indicated by

examples given below, the use of 2 equiv. of $Cu(OAc)_2$ often provides higher yields of amination products at lower temperature, without requiring any additional reagents such as *N*-methylmorpholine *N*-oxide (Scheme 111).

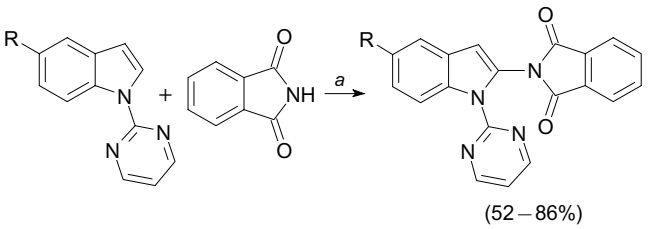
Scheme 111



(*a*) $Cu(OAc)_2$ (2 equiv.), DMSO, 60 °C, 12 h (28 – 89%);
(*b*) $Cu(OAc)_2$ (25 mol.%), NaOAc (2 equiv.), NMO (3 equiv.), DMSO, 100°C; R = H, 2-CF_3, 3-CF_3, 4-CF_3, 4-Cl, 4-F, 3-Ac, 3-CO_2Me, 3-Ph, 3-OCF_3, 4-Bu^t, 4-OMe, 4-SMe, 4-CO_2Me

The introduction of a 2-pyrimidyl substituent to the nitrogen atom contributes to the activation of the C – H bond in position 2 of indole towards Cu-catalyzed amidation.[320] The yields of the reaction products considerably depended on the nature of substituent in position 5 of the heterocycle: the lowest yields (0 and 31%) were obtained for R = CN and NO_2 (Scheme 112).

Scheme 112

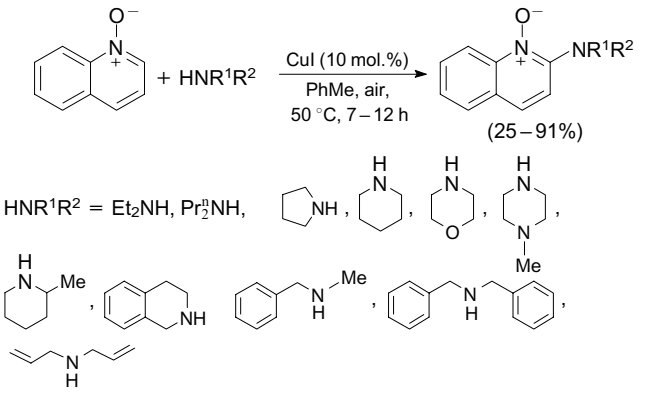


(*a*) CuOAc (20 mol.%), PhMe – 1,2-dichlorobenzene (1 : 1), O_2, 150 °C; R = H, Me, F, Cl, Br, OMe

Study of amination of quinoline *N*-oxides and their derivatives in the presence of catalytic amounts of CuI demonstrated that these reactions take place for secondary cyclic and linear aliphatic amines (Scheme 113).[321] The amination is directed to position 2 of the heterocycle, and the yields of products considerably depend on the structure of amines.

The same issue was addressed by Sun and co-workers,[322] who carried out both the amination and amidation of

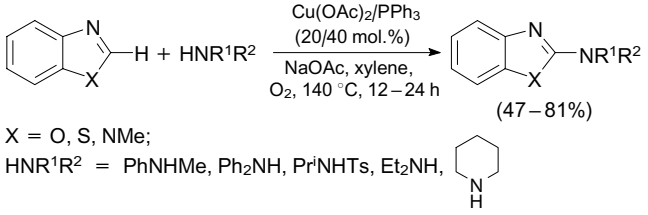
Scheme 113



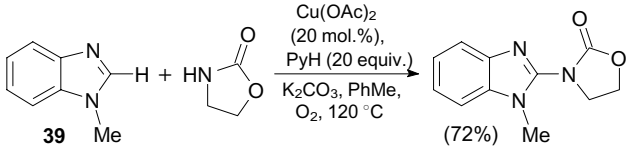
quinoline *N*-oxides with cyclic secondary amines and caprolactam. Catalysis was performed by 10 mol.% copper acetate in the presence of 2 equiv. of silver carbonate; the reaction proceeded in benzene at 120 °C.

Mori and co-workers[323] reported the direct amination of azoles into position 2 using copper acetate with the triphenylphosphine ligand as a catalyst and air oxygen as an oxidant (Scheme 114). The reaction was carried out for *N*-methylaniline, diethylamine, sulfonamides and other amine components.

Scheme 114



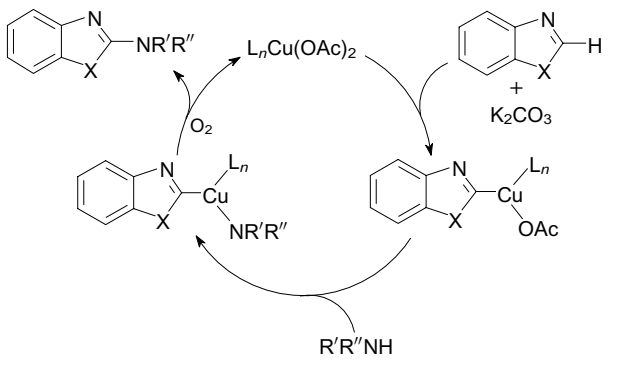
Scheme 115



Similar conditions were used by Wang and Schriber[324] to carry out amidation of benzimidazole **39** (Scheme 115).

The catalytic cycle proposed for this reaction (Scheme 116) includes deprotonation of azole **39** to give organocopper compound, ligand exchange and reductive elimination to give the target product. The resulting Cu^I is oxidized with oxygen to Cu^{II}. However, the nature of copper formed after the reductive elimination and the possibility of oxygen-induced formation of Cu^{III} are not discussed in the paper.

Scheme 116

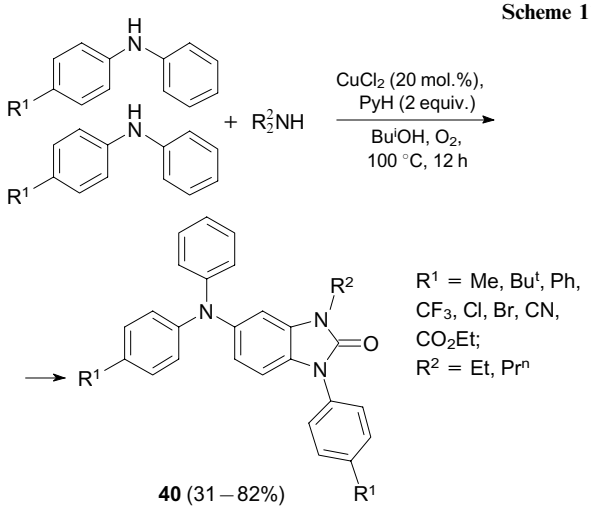


An interesting method of amination of benzoxazole in position 2 is the reaction with a number of tertiary amines of type $R^1R^2NCH_2R^3$, such as trialkylamines, tribenzylamine, triallylamine, *N*-methylmorpholine, *N*-benzylmorpholine and *N*-benzylpiperidine.[325] The reaction is carried out in the presence of 10 mol.% $CuBr_2$ and 20 mol.% acetic acid in dioxane in an oxygen atmosphere at 120 °C. As a result, the R^1R^2N moiety is involved in amination, while CH_2R^3 is converted to the corresponding aldehyde

(R^3CHO). It was shown that the amination of benzoxazole and its derivatives with secondary amines can be catalyzed by 20 mol.% copper(II) acetate in the presence of 2 equiv. of acetic acid in acetonitrile in an oxygen atmosphere at 70 °C.[326] In addition, a method was developed for introducing an amino group into these substrates on treatment with dimethyl- and diethylformamide in the presence of 20 mol.% copper(II) acetate and benzoic acid.

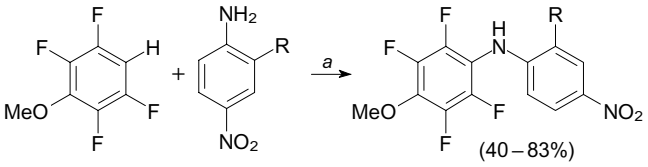
In some cases, amino-substituted heterocycles were formed as a result of unexpected cascade processes. For example a series of polysubstituted imidazolones **40** was obtained by the reaction of several diarylamines with diethylamine and dipropylamine (Scheme 117).[327] The authors assumed a complex multistep mechanism, the key step of which is a tandem double C – H amination.

Scheme 117



Arenes containing an 'acidic' C – H bond, *e.g.*, perfluorinated compounds, can also be aminated in the presence of the $Cu(OAc)_2$ catalyst to give products in good yields.[328] In this case, the O_2 – TEMPO system is used as the oxidant (Scheme 118).

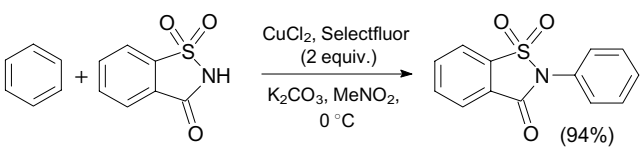
Scheme 118



(*a*) $Cu(OAc)_2$ (20 mol.%), ButOK, TEMPO, DMF, O_2, 40 °C, 24 h; R = H, Me, Cl, OMe

The known arylation of saccharin with unsubstituted benzene[329] was accomplished under mild conditions in the presence of $CuCl_2$ catalyst under the action of a special oxidant Selectfluor — 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Scheme 119).[330] Note an attempt to carry out the amidation of arenes using photocatalysis, for example, with ruthenium complexes.[331]

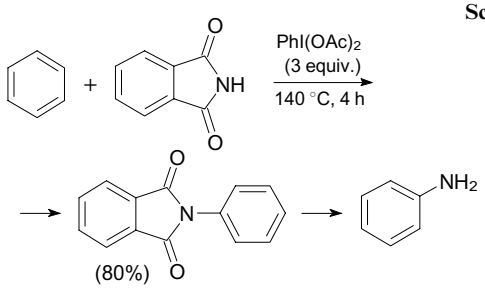
Scheme 119



5.2. Miscellaneous methods for conduction of C – H-amination

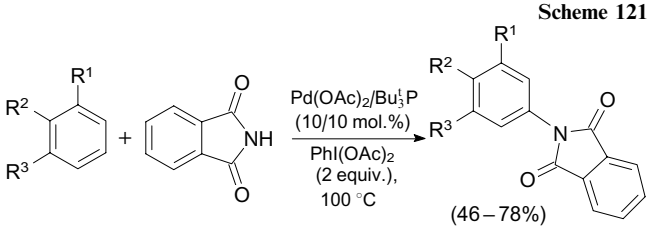
Especially popular is the imidation of benzene with phthalimide, which was studied in the presence of various metals and oxidants.[332] An example of the metal-free oxidative version of this reaction is shown in Scheme 120.

Scheme 120



In 2013, Hartwig and co-workers[333] carried out this reaction for methyl- and methoxy-substituted arenes with a palladium catalyst using hypervalent iodine as the oxidant (Scheme 121).

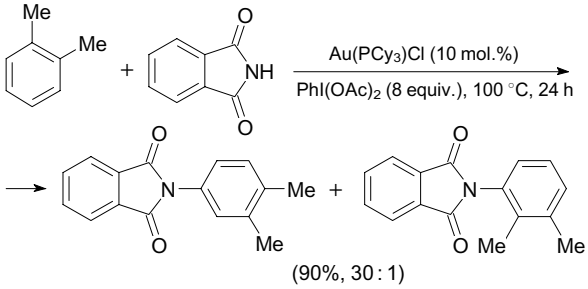
Scheme 121



R1 = Me, Cl; R2 = Me, OMe, F, Cl, Br, I; R3 = H, Me

DeBoef and co-workers[334] carried out the same reaction using catalysis by Au^I complex, which was oxidized to Au^{III} (Scheme 122). *o*-Xylene, acting as both a reactant and a solvent, is imidated into position 4 with high regioselectivity. The reaction is carried out in the presence of trialkylphosphines as ligands, the most effective of which is tricyclohexylphosphine.

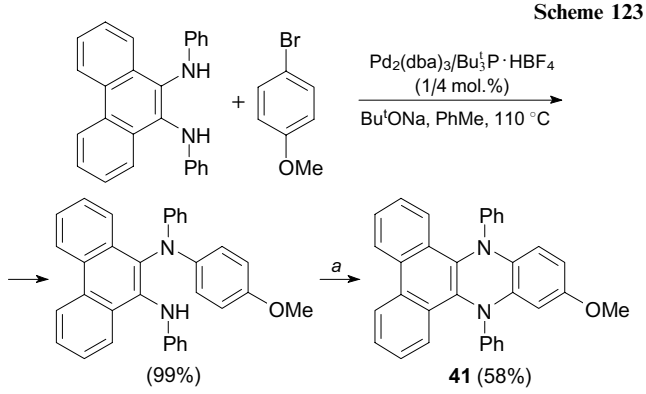
Scheme 122



An imidation method for five-membered heterocycles such as pyrrole, thiophene, benzothiophene, oxazole and benzoxazole on treatment with ditosylamines in the presence of *N*-bromosuccinimide has been developed.[335] Chen

and co-workers [336] synthesized 9,14-diaryl-9*H*-dihydrodibenzo[*a*,*c*]phenazine (**41**) by using both methods for C(sp^2) – N formation: the palladium-catalyzed Buchwald – Hartwig reaction and the copper-catalyzed intramolecular amination (Scheme 123). In this interestingly designed synthesis, the second step is carried out using an excess of copper acetate.

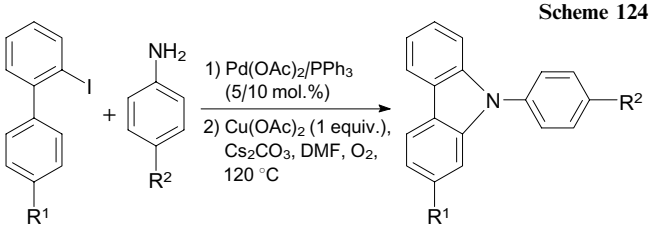
Scheme 123



(*a*) $Cu(OAc)_2$ (2 equiv.), DMSO, O_2, 120 °C

One more reaction in which a palladium catalyst was used in the first step and two C – N bonds were successively formed was described by Song and co-workers.[337] The reaction involved 2-iodobiphenyl and a number of (hetero)-aromatic amines. This gave an extensive series of *N*-(hetero)arylcarbazoles, and it was shown that the substituents in aniline have a greater influence on the course of the reaction than the substituent in 2-iodobiphenyl (Scheme 124).

Scheme 124



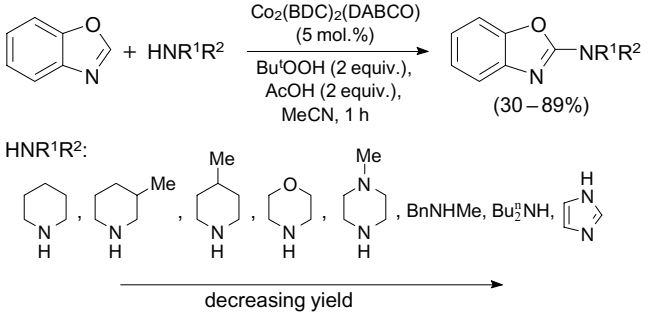
R^2 = H: R^1 = H, Me, Bu^t, OMe, Ph, F, NO_2, CHO (63 – 92%);
R^1 = H: R^2 = H, Me, Pr^i, SMe, CN, Ac, CO_2Me, F, Cl, Br (36 – 92%)

The vast majority of the described oxidative amination reactions are carried out in the presence of Cu^{II}. However, the applicability of catalytic systems based on other metals is being actively studied. For example, the Rh^{III} complex with 2-methylquinoline was used for C – H-amination of *N*-pentafluorophenylbenzamide in the *ortho*-position with several cyclic secondary amines,[338] for sulfonamidation of 1,2-bis(1-phenylethylidene)hydrazine and analogous substituted azines,[339] and also for amination and sulfonamidation of indoles.[340] Catalysis by Ir^{II} compounds allows for the amination of substrates containing amide directing groups using both aliphatic [341] and aromatic amines;[342] iridium-catalyzed amidation of tetrazines was also recently described.[343] Quite a number of recent studies were devoted to amidation, especially under the action of sulfoximines, catalyzed by complexes of various metals, for example iridium.[344] In these reactions, additives are necessarily used, most often, of silver or copper salts. Expansion of the range of catalytic systems makes it possible to vary the reactant structure, control the regioselectivity of reactions and carry out reactions under milder conditions.

5.3. Immobilized catalysts in C – H-amination

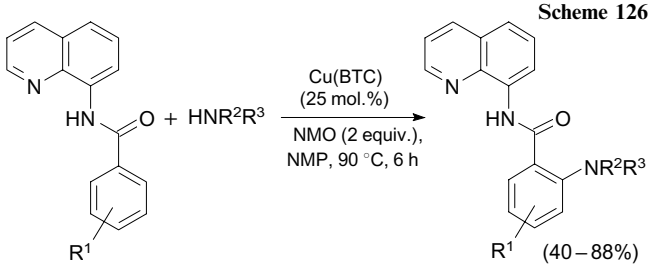
Unlike C – N bond formation reactions that use aryl halides or arylboronic acids, the oxidative C – H-amination reactions are rarely conducted with immobilized catalysts. Until recently, almost no such studies were known, as follows from a review of Vaccaro and co-workers [345] published in 2016. The use of copper MOF based on biphenyl-4,4′-dicarboxylic acid with 1,4-diazabicyclo[2.2.2]octane (DABCO) made it possible to perform the amidation of heteroaromatic compounds,[346] while the amination of benzoxazole was catalyzed by another cobalt-containing MOF.[347] Depending on the nature of the amine, the yields of products in the former case varied from medium to high and decreased in the series shown in Scheme 125.

Scheme 125

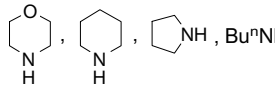


In an earlier publication, the same authors [304] demonstrated the applicability of copper-containing MOF Cu(BTC) (BTC is benzene-1,3,5-tricarboxylic acid) for the amination of aromatic compounds with a 8-aminoquinoline directing group. The product yields of this reaction are also highly scattered; the catalyst should be added in an amount of 25 mol.%, and *N*-methylmorpholine *N*-oxide is used as an oxidant (Scheme 126).

Scheme 126

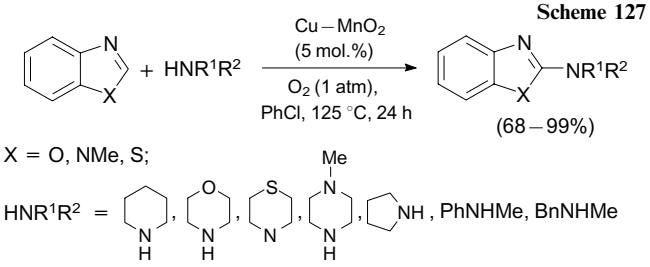


R^1 = H, 4-OMe, 3-Me, 2-CF_3, 3-CF_3, 4-CF_3;

HNR^2R^3 =  , Bu^nNH_2, PhNHMe, BnNHMe

The efficiency of γ-MnO_2 catalysis for the C – H-amination of benzoxazole and its derivatives in the presence of oxygen was reported;[348] the addition of a slight amount of copper to this oxide expanded the scope of applicability of the catalyst: the oxidative amination was conducted not only for benzoxazole, but also for other heterocycles such as benzimidazole, benzothiazole, oxazole and thiazole

Scheme 127



(Scheme 127).[349] The reactions were carried out in chlorobenzene at 125 °C in an oxygen atmosphere.

6. Conclusion

This review was meant to demonstrate the substantial progress made in the studies of cross-coupling reactions in relation to the C(sp^2) – N bond formation, which is the most intricate reaction among the given class. Whereas at the end of the 20th century, palladium catalysis enabled conduction of reactions of aryl halides with various amines (Buchwald – Hartwig amination), in the beginning of the 21st century, extensive studies of the catalytic Ullmann reaction (Goldberg reaction in the case of amides) already started, in which expensive palladium catalysis was successfully replaced by copper catalysis with less expensive ligands. There appeared a new approach to the formation of carbon – heteroatom bond — Chan – Lam reaction, in which the Cu^{II}-catalyzed cross-coupling occurs between arylboronic acids and nucleophiles such as amines and amides. The new method opened up unique prospects for the synthesis of nitrogen-containing compounds under mild conditions in the presence of weak bases and without ligands. Finally, apart from involvement of C(sp^2) – Hal and C(sp^2) – B bonds in coupling reactions, there appeared the possibility of direct functionalization of the C(sp^2) – H bond in arenes and heteroarenes based on the metallation of these substrates followed by oxidative functionalization. This field is being developed very extensively. Note that synthetic advances in the new fields are often ahead of mechanistic studies, and we did not pay much attention to the mechanisms either. However, since the pathways to reaction products in reactions catalyzed by palladium and (especially) copper complexes have been interpreted by mechanisms involving high-valence Pd^{IV} and Cu^{III} transition states or intermediates and since differences in these mechanisms influence the reaction selectivity, which is very important, we refer readers to a relevant review[350] published in *Nature* to get acquainted with this problem. Undoubtedly, in the very near future, one should expect new discoveries and achievements related to the most important type of cross-coupling reaction, that is, carbon – nitrogen bond formation.

This review was prepared with the financial support of the Russian Foundation for Basic Research (Project No. 19-13-50173).

7. List of abbreviations

The following abbreviations and designations are used in the review:

acac — acetylacetonate,
Ad — adamantyl,
AzH — azole,
Asc — ascorbate,
BDC — terephthalic acid,
BINOL — 1,1′-bi-2-naphthol,
BINAP — 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl,
Bpy — 2,2′-bipyridine,
BTC — benzene-1,3,5-tricarboxylic acid,
ChCl – Gly — choline chloride and glycerol,
CPME — cyclopentyl methyl ether,
Cy — cyclohexyl,
DABCO — 1,4-diazabicyclo[2.2.2]octane,
DavePhos — 2-(dimethylamino)-2′-(dicyclohexylphosphino)biphenyl,
DBU — 1,8-diazabicyclo[5.4.0]undec-7-ene,
dba — dibenzylideneacetone,
DHAQ — 1,4-dihydroxy-9,10-anthraquinone,
DMAP — 4-(dimethylamino)pyridine,
DME — dimethoxyethane,
dppe — 1,2-bis(diphenylphosphino)ethane,
dppf — 1,1′-bis(diphenylphosphino)ferrocene,
Fu — furyl,
GO — graphene oxide,
Hex — hexyl,
HMDS — bis(trimethylsilyl)amide,
Me_2Bpy — 4,4′-dimethyl-2,2′-bipyridine,
MNPs — magnetic nanoparticles,
MOF — metal-organic framework,
MS — molecular sieves,
Ms — methanesulfonyl (mesyl),
MW — microwave (irradiation),
Naph — naphthyl,
NHC — N-heterocyclic carbenes,
NMO — 4-morpholine *N*-oxide,
NMP — *N*-methyl-2-pyrrolidone,
NPs — nanoparticles,
Oct — octyl,
PANI — polyaniline,
PEG — polyethylene glycol,
Phen — 1,10-phenanthroline,
PS — polystyrene,
PVA — polyvinyl alcohol,
L-Pro — L-proline,
Py — pyridyl,
rt — room temperature,
Tf — trifluoromethanesulfonyl (triflyl),
TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TMEDA — tetramethylethylenediamine,
TMS — trimethylsilyl,
TCT — (3-chloropropyl)trimethoxysilane,
Tol — methylphenyl (tolyl),
Ts — *p*-toluenesulfonyl (tosyl).

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