



TRANSITION METAL-CATALYZED SYNTHESIS OF FUNCTIONALIZED ARENES UNDER SOLVENT-FREE CONDITIONS

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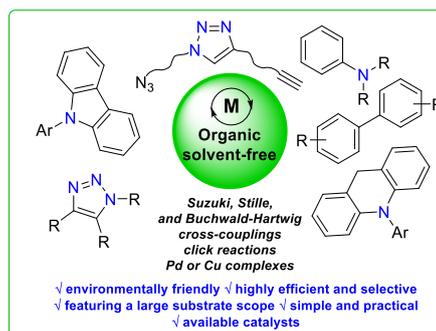
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Abstract

The present review is devoted to a versatile and ecologically friendly method for the formation of carbon–carbon and carbon–nitrogen bonds in the synthesis of aromatic and heteroaromatic compounds that exhibit the high potential of application in the most innovative fields of science and engineering under conditions of solvent-free catalysis by transition metal complexes.



Key words: green chemistry, cross-coupling reactions, click reactions, solvent-free synthesis, homogeneous catalysis.

1. Introduction

Current progress in the chemical industry featuring an extremely high level and rate of creation of new knowledge-intensive technologies has led to a radical transformation of traditional principles of organic synthesis. In the last decade, particular attention has been drawn to the development of wasteless chemical technologies that are based on the available raw materials and the application of environmentally benign synthetic methodologies in combination with the high efficiency and low prime cost. Nowadays, one of the most promising approaches that meet the above-mentioned requirements is catalysis by transition metal complexes. The transition metal-catalyzed carbon–carbon and carbon–heteroatom bond-forming reactions in the synthesis of aromatic and heteroaromatic compounds that show high potential for the application in innovative fields of science and engineering have already gained considerable importance in fine organic synthesis and the production of pharmaceuticals, natural compounds, constructional materials, and materials for organic electronics [1]. These catalytic processes provide an opportunity to exclude the chemical reagents that cause the formation of hazardous wastes and to obtain in the more shortly way the target products with the maximum efficiency and selectivity [2].

The use of organic solvents in most chemical processes has the highest negative impact on the environment [3, 4] comprising nowadays the largest part of the resulting chemical wastes (up to 80%). The high material and energy expenditures, which are required for the utilization of large volumes of solvents (often highly toxic), multiply increase the value of the target products. A reduction in the volume of conventional organic solvents, their substitution for ecologically friendly ones [5], or, ideally, their full absence in the reaction medium can not

only significantly minimize the mentioned problems but also improve the technologically important parameters owing to a reduction in the catalyst loading, an increase in the reaction rate, and, as a consequence, an increase in the efficiency of the whole chemical process [6]. An urgent task is the development of new and improvement of the existing metal-catalyzed methods for the formation of carbon–carbon and carbon–heteroatom bonds in water without the use of organic solvents [7]. A successful solution of this problem would enable considerable progress in the realization of a nature preservation strategy and sustainable development and simultaneously facilitate the realization of priority directions of scientific and technological development of the Russian Federation for a transition to new materials and countering to the man-made hazards owing to the creation of new technologies that do not utilize toxic and inflammable solvents.

2. Palladium-catalyzed cross-couplings in water

Nowadays, palladium-catalyzed cross-couplings amount to one of the most important and popular methods for the construction of C–C, C–N, C–O, and C–B bonds in aromatic compounds [8, 9]. Over a few years, cross-couplings were one of the main tools in the synthesis of pharmaceuticals [1], components for organic light-emitting diodes (OLEDs) [10] and solar cells [11]. The paramount importance of the industrially implemented palladium-catalyzed processes promotes a further search for efficient conditions for cross-couplings which would enable the synthesis of intermediate compounds and final products in the maximum yields and with the minimum wastes.

One of the most pressing challenges of organic synthesis for many years still remains the displacement of organic solvents

for water. The use of water in organic synthesis instead of organic solvents is reasonable both from the ecological and economic points of view. Palladium-catalyzed reactions in water offer a range of considerable advantages: reduced organic wastes and exclusion of dangerous reaction conditions. Furthermore, being one of the most popular solvents, water can promote catalysis owing to solvation effects, which simplify the metal insertion into the carbon–(pseudo)halogen bond, and protect the catalyst from a possible displacement of labile ligands in the metal coordination sphere. The application of water as a solvent can considerably simplify the isolation and purification of products and the catalyst regeneration. It is also noteworthy that, unlike conventional organic media, water is the cheapest, nontoxic, and nonflammable solvent.

Suzuki–Miyaura cross-coupling in the synthesis of bis(hetero)aryl compounds in water

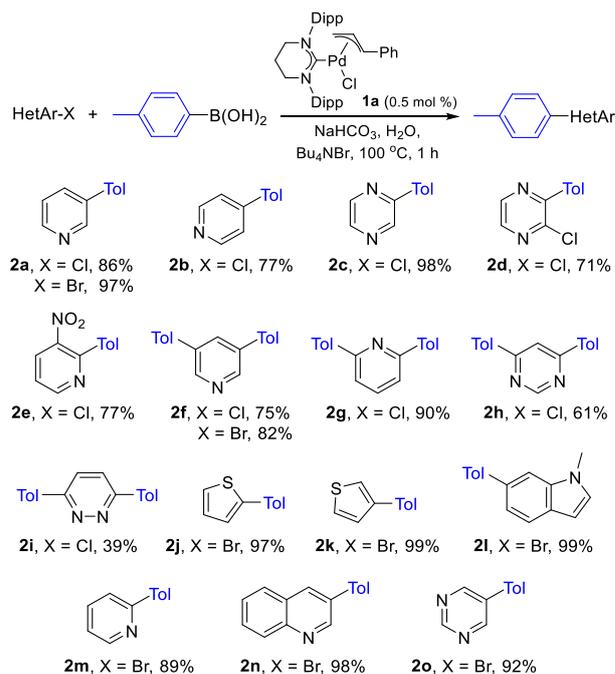
The $C_{Ar}-C_{Ar}$ couplings catalyzed by transition metal complexes represent fundamental transformations in modern organic chemistry. This strategy gives access to various bi(hetero)aryl compounds which can serve as main building blocks in the synthesis of pharmaceuticals and agrochemicals, ligands for asymmetric synthesis, and functional materials. The Suzuki–Miyaura reaction catalyzed by palladium complexes is one of the most efficient methods for the synthesis of bis(hetero)aryls of both symmetrical and unsymmetrical structures. The major advantages of this reaction include mild conditions and commercial availability of different boronic acid derivatives, which are more preferential from the ecological point of view than other organometallic cross-coupling reagents. Despite the substantial advances in this field achieved with conventional organic solvents, the Suzuki–Miyaura reaction in an aqueous medium still has several limitations. Most of the modern catalytic conditions imply the use of a mixture of water with one or another organic solvent rather than neat water [3, 12, 13]. Furthermore, the introduction of some heterocyclic compounds, for example, heterocyclic halides is still challenging [1, 14–17].

The palladium-catalyzed cross-couplings in an aqueous medium involving aromatic bromides and iodides were studied for the first time by Prof., full member of the Russian Academy of Sciences I. P. Beletskaya and coauthors in the late 1980s [18].

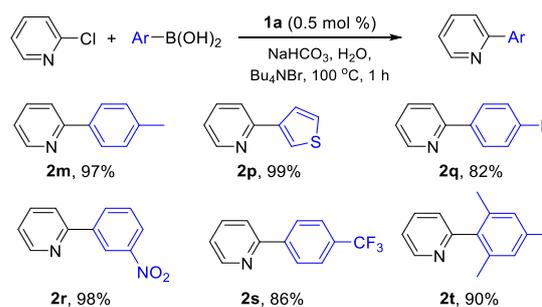
In 2013, the application of catalytic systems based on highly active and readily available palladium complexes of *N*-heterocyclic carbenes (NHC) was shown to enable the Suzuki–Miyaura cross-coupling of low active (hetero)aryl chlorides with (hetero)arylboronic acids in an aqueous medium (Scheme 1) [19]. This work reported the first example of the Suzuki–Miyaura reaction in an aqueous medium involving heterocyclic chlorides based on pyrimidine, pyrazine, and pyridazine. It should also be noted that, independent from the nature and position of the substituent in an aromatic core of the arylboronic acid, the corresponding cross-coupling products were obtained in the yields close to quantitative.

The successful synthesis of thiophene-containing compound **2p** showed a possibility of application of the suggested conditions for the heteroaryl–heteroaryl couplings (Scheme 2).

The developed conditions provide reactions with simplicity, efficiency, and ecological safety and offer the following advan-



Scheme 1. Interaction of heteroaryl halides with 4-tolylboronic acid.



Scheme 2. Reactions of 2-chloropyridine with arylboronic acids.

tages. Firstly, the reactions can be accomplished in neat water without recourse to organic cosolvents and do not require preliminary degassing and an inert atmosphere. Secondly, the couplings utilize a cheap and nonhazardous base, namely, NaHCO_3 . Finally, the reactions require only insignificant amounts of a phase-transfer catalyst (Bu_4NBr).

Suzuki–Miyaura cross-coupling in the synthesis of 1,4,5-trisubstituted 1,2,3-triazoles in water

Over the past decade, 1,2,3-triazoles found extensive use in medicinal chemistry [20, 21] and the synthesis of new functional materials [22, 23]. The main method for obtaining 1,2,3-triazoles is the copper-catalyzed 1,3-dipolar cycloaddition of azides to terminal alkynes (CuAAC or "click" reaction) [22, 24, 25]. This method opens the way to 1,4-disubstituted 1,2,3-triazoles with high selectivity. However, for the synthesis of fully substituted triazoles, which represent more valuable research objects, it requires significant modifications connected with the selective introduction of additional substituents, especially aromatic groups. The need to increase the number of steps, the use of hardly accessible organometallic reagents and expensive catalysts, and the absence of reliable and safe

experimental protocols seriously restrict the availability of 1,4,5-trisubstituted 1,2,3-triazoles.

The efficiency and applicability of the catalytic conditions elaborated for the synthesis of biaryls by the Suzuki–Miyaura reaction in water [19] were studied for the cross-coupling of 4- and 5-halotriazoles with arylboronic acids in order to produce the corresponding 4- and 5-substituted 1,2,3-triazoles [26].

Using the model reaction of 4-bromo-5-methyl-1-phenyl-1,2,3-triazole with 4-methylphenylboronic acid, it was established that, as well as in the synthesis of the biaryl compounds, the palladium complex (6-Dipp)Pd(cinn)Cl (**1a**) appeared to be the most efficient catalyst for this process. The highest yield of product **3a** (97%) was achieved upon refluxing of the reaction mixture in water for 8 h in the presence of 1 mol % of **1a**, 10 mol % of Bu₄NBr, and two equivalents of KOH.

The optimized conditions were further used to define the application scope of the suggested method for a broad range of 4- and 5-halo-1,2,3-triazoles and (hetero)arylboronic acids (Schemes 3 and 4). The catalytic method for the synthesis of fully substituted 1,2,3-triazoles bearing different alkyl, aryl, and heteroaryl groups at 1, 4, and 5 positions affords high or almost quantitative yields. These conditions enable the Suzuki–Miyaura reaction in water involving 4- and 5-chlorotriazoles (including low active 4- and 5-chlorotriazoles) and (hetero)arylboronic acids.

The highly efficient catalytic system devised based on the available palladium(II) NHC complexes featuring cinnamyl ligands is capable of catalyzing the Suzuki–Miyaura reaction of different heteroaryl halides and halotriazoles with (hetero)arylboronic acids in an ecologically friendly aqueous medium without the use of organic cosolvents.

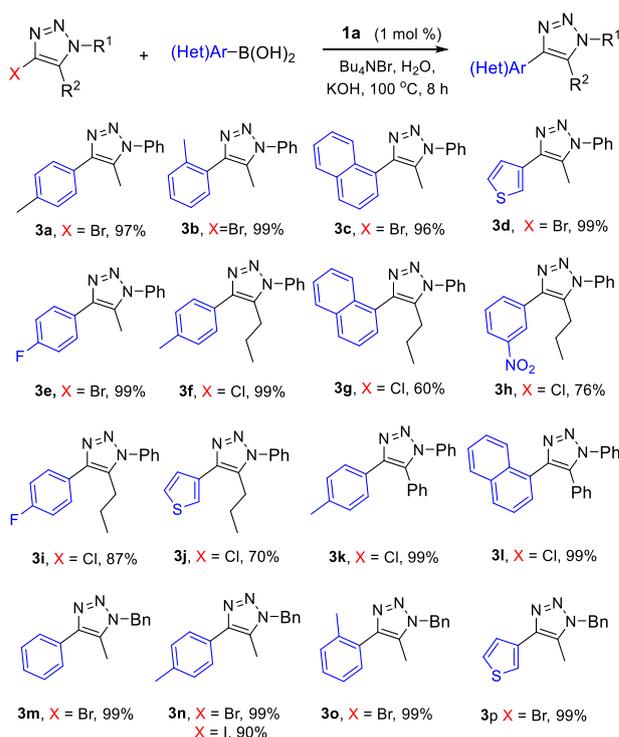
3. Solvent-free palladium-catalyzed cross-couplings

The application of organic solvents makes a major contribution to the formation of wastes in organic synthesis. The ecological compatibility of processes is assessed using Sheldon's *E* factor which is defined as a ratio of the mass of organic wastes (kg) to the mass of the resulting product (kg) [27]. For many pharmaceuticals, the values of *E* factor exceed 100 [28]. The main contribution to an increase in the *E* factor is made by organic solvents, many of which are toxic for humans and the environment and require expensive regeneration. A reduction in the value of *E* factor of chemical processes is one of the most important objectives of green chemistry. The development of new efficient methods of organic synthesis without the use of solvents is an urgent task of modern chemistry. The complete rejection of organic solvents at all stages, including synthesis and purification of products, can reduce the value of *E* factor by one or two orders of magnitude.

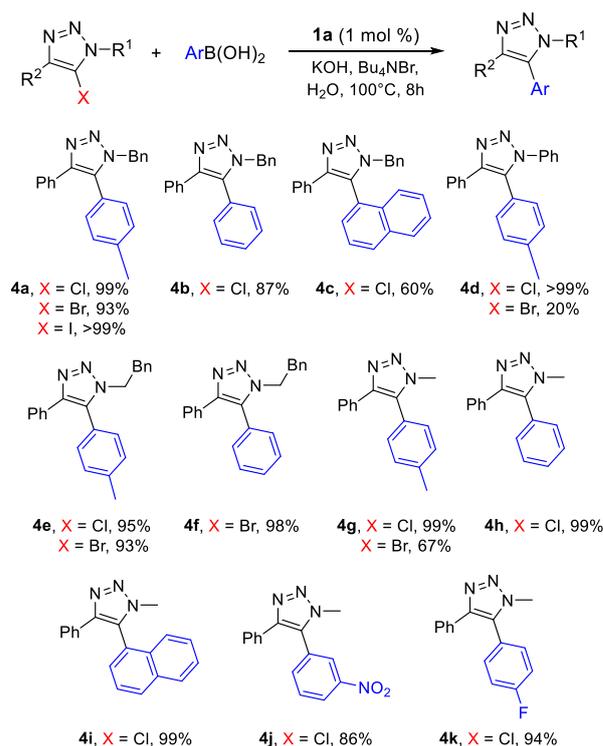
Solvent-free Suzuki–Miyaura reaction

One of the key challenges of solvent-free organic reactions is the homogeneity of a reaction medium. To address this issue, pinacol esters of arylboronic acids ArBPIn are used as organoboron reagents in the Suzuki–Miyaura cross-coupling, which often represent liquids or low-melting compounds.

The highest activity in the solvent-free Suzuki–Miyaura



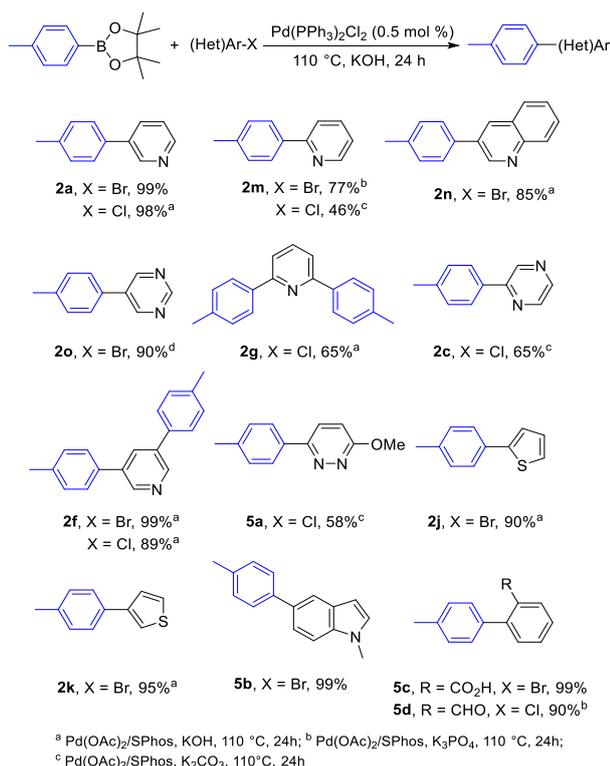
Scheme 3. Cross-coupling of 4-halotriazoles in water.



Scheme 4. Cross-coupling of 5-halotriazoles in water.

reaction was observed for the systems Pd(OAc)₂/SPhos/KOH and (Ph₃P)₂PdCl₂/KOH that provided the highest yields of cross-coupling product **2a** (Scheme 5) [29].

The application scope of the suggested method was studied on a large series of (hetero)aryl halides (Scheme 5). (Ph₃P)₂PdCl₂ provided excellent yields of the products of cross-couplings between a pinacol ester of *p*-tolylboronic acid and different (hetero)aryl bromides bearing electron-donating,



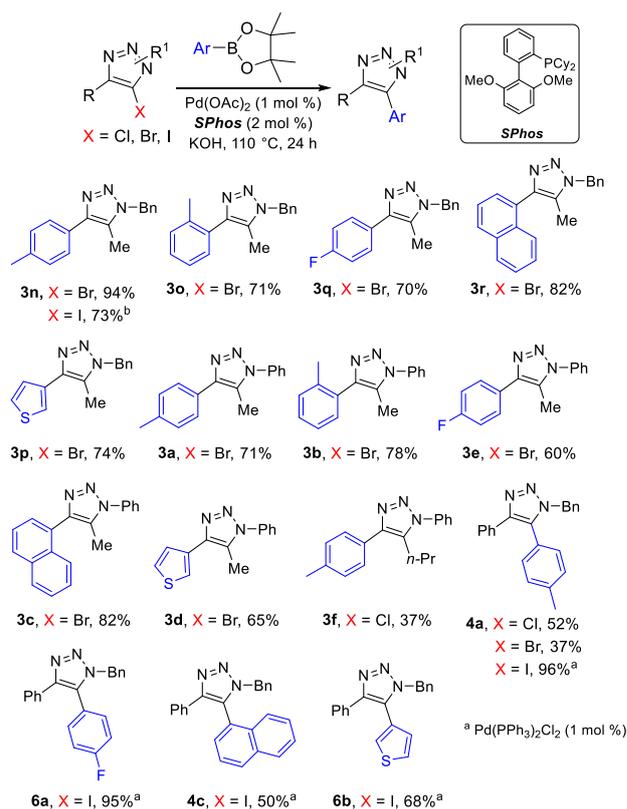
Scheme 5. Cross-coupling of (hetero)aryl halides.

electron-withdrawing, and sterically hindered substituents under solvent-free conditions (110 °C, KOH). The most efficient system for (hetero)aryl chlorides appeared to be Pd(OAc)₂/SPhos.

This approach was also successfully adapted for the Suzuki cross-coupling of more complicated substrates such as halogen-substituted 1,2,3-triazoles (Scheme 6) [30]. Thus, the highest efficiency in the reactions of chloro- and bromo-1,2,3-triazoles was demonstrated by the catalytic system Pd(OAc)₂/SPhos, whereas in the case of highly reactive iodo-1,2,3-triazoles (Ph₃P)₂PdCl₂ was the most active catalyst. The developed synthetic protocol can be readily scaled up with no significant loss in the efficiency.

Solvent-free Buchwald–Hartwig reaction

The Buchwald–Hartwig amination of aryl halides is another powerful tool in organic chemistry that enables the formation of a carbon–nitrogen bond and is widely used both in medicinal chemistry and in the synthesis of functional materials. Among a variety of methods developed to date, only a few examples deal with the solvent-free protocols [31–36]. The first one was described by Prof. I. P. Beletskaya and coauthors in 2003 for the amination of aryl bromides catalyzed by Pd(OAc)₂/DPEphos [31]. In 2004, the group of Prof. M. Yoshifuji reported the synthesis of a diphosphinidene cyclobutene palladium complex and its application in the solvent-free amination [32]. This complex exhibited high activity in the amination of aryl halides with primary amines. Despite the high performance of this complex in the synthesis of secondary amines, its efficiency for the production of tertiary amines was much lower. In 2011 and 2013, Beccalli *et al.* reported the solvent-free *N*-arylation of indolines [33, 36]. The reaction was promoted both by heating and microwave irradiation. The method provided low yields of



Scheme 6. Cross-couplings of 4- and 5-halo-1,2,3-triazoles with arylboronic acid pinacol esters.

the target products and low conversions of the starting aryl bromides. Later the groups of Prof. Stradiotto [34] and Nolan [35] performed the reactions with aromatic and heteroaromatic chlorides. For this purpose, the more efficient palladium-based catalytic systems were developed. However, most of the described couplings afforded low yields (especially in the case of aryl chlorides) and were severely restricted by a substrate scope.

A series of palladium complexes containing simultaneously *N*-heterocyclic carbene and phosphine ligands were developed in 2019 (Scheme 7) [37]. The method included the treatment of complex **1a**, the most active catalyst for the amination [38], with hydrogen chloride in dioxane to remove a cinnamyl ligand and quantitatively afforded corresponding dimeric intermediate **7** which, then, was reacted with tertiary phosphines differing in the donor properties and steric volumes.

The catalytic activity of the new complexes was studied in the solvent-free amination using the following model reactions: the interaction of 1-bromonaphthalene with aniline (primary amine) and *p*-bromoanisole with diphenylamine (secondary amine). The highest activity was demonstrated by complex **8b** bearing SPhos ligand (Table 1).

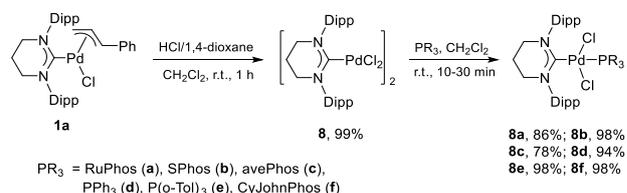
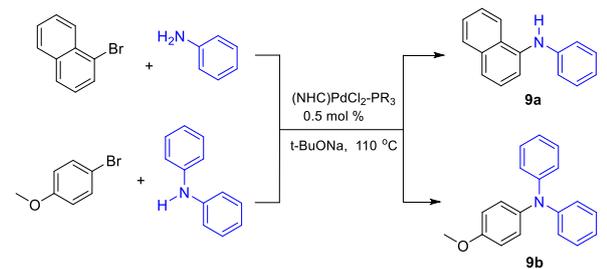
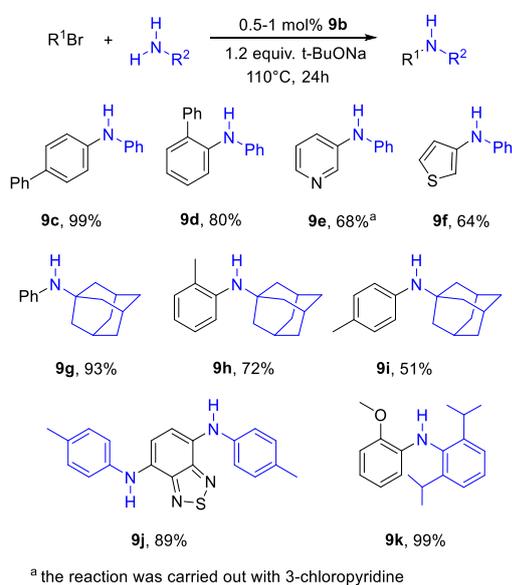
Scheme 7. Synthesis of mixed ligand complexes (6-Dipp)(R₃P)PdCl₂.

Table 1. Catalytic performance of complexes **8a–f** in the reactions with primary and secondary amines


Entry	Catalyst 9 (PR ₃)	Yield, %	
		9a	9b
1	8a (RuPhos)	86	93
2	8b (SPhos)	98	95
3	8c (DavePhos)	86	84
4	8d (PPh ₃)	48	15
5	8e [P(<i>o</i> -Tol) ₃]	98	14
6	8f (CyJohnPhos)	98	70

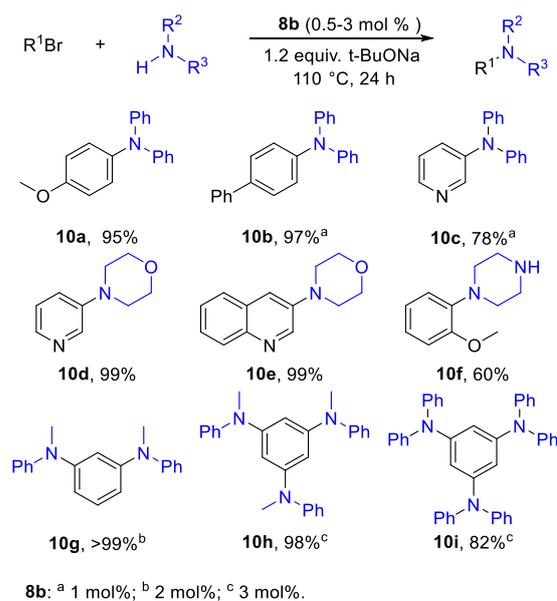
It is interesting to note that the activities of complexes **8a–f** were in good agreement with the donor properties of the phosphine ligands (according to the ³¹P NMR spectroscopic data) and reduced in the following series: **8b** (SPhos) > **8a** (RuPhos) > **8c** (DavePhos) > **8d** (CyJohnPhos) > **8e** (PPh₃) > **8f** [P(*o*-Tol)₃].

Complex **8b** promoted the reactions of different primary and secondary amines. It was found that the cross-coupling of primary amines leads to a series of diarylamines in high yields (Scheme 8).

**Scheme 8.** Cross-coupling of primary amines.

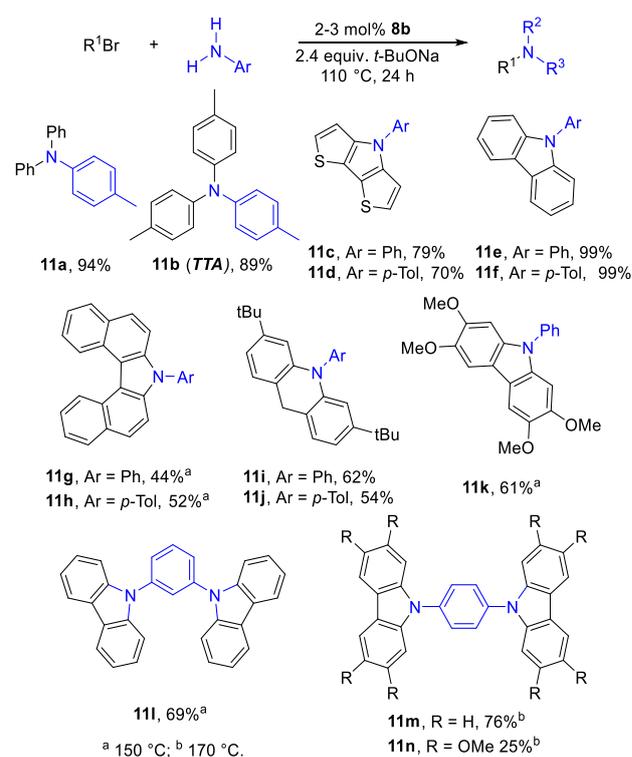
The developed catalytic system was also efficient in the case of sterically hindered aryl bromides (see, for example, compounds **9d**, **9h**, and **9k**) and heteroaryl halides (products **9e**, **9f**, and **9j**).

The double amination of dibromobenzothiadiazole provided the efficient synthesis of compound **9j** which nowadays is used in the design of conjugated polyanilines exhibiting unique optoelectronic properties [39, 40].

**Scheme 9.** Cross-coupling of secondary amines.

The results of the arylation of secondary amines with mono-, di- and trihalo(hetero)arenes are presented in Scheme 9. All the products were isolated in high and often quantitative yields. This indicates the high performance of complex **8b**.

Of particular interest is a possibility of application of the developed catalytic system for the one-pot synthesis of industrially relevant triarylamines by double arylation of primary amines. Tritolylamine **11b** (TTA), extensively used in electronics as a semiconductor with hole conductivity [41, 42], and a series of planar polyaromatic systems, highly popular in OLED technologies, can be readily obtained using this synthetic strategy (Scheme 10).

**Scheme 10.** Double arylation of arylamines.

The chosen reaction conditions can also be applied for the synthesis of *N*-arylcarbazoles, which shows the possibility of the realization of two sequential intramolecular arylations of primary and secondary amines. It should be noted that, besides unique thermal, electronic, and optical properties [43–46], the carbazole derivatives exhibit a broad spectrum of biological activities [47, 48]. The amination of 2,2'-dibromobiphenyl with aniline and *p*-toluidine gave rise to corresponding *N*-arylcarbazoles **11e** and **11f** in almost quantitative yields. In the case of high-melting dibromobiaryls, the reaction required heating to 150 or 170 °C for completion (Scheme 10); therewith, the efficiency of the catalyst did not reduce. Under the same conditions, dibenzocarbazoles **11g** and **11h** were generated in 44 and 52% yields, respectively. It should be noted that there had been only one earlier report on the synthesis of carbazole **11g** where the yield of the target product was only 1% [49].

The derivatives of dithieno[3,2-*b*:2',3'-*d*]pyrrole **11c** and **11d** were isolated in 70 and 79% yields, respectively. These compounds also feature unique physical properties [50, 51]. The main method for their synthesis is the palladium-catalyzed ($\text{Pd}_2(\text{dba})_3/\text{PrtBu}_3$ [52] or $\text{Pd}_2(\text{dba})_3/\text{BINAP}$ [53]) intermolecular amination of 3,3'-dibromo-2,2'-bithiophene in toluene. The developed solvent-free methodology afforded these compounds in the yields comparable to those achieved by other cross-coupling methods in toluene. Of note is also the synthesis of dihydroacridines **11i** and **11j**, which serve as valuable building blocks for the preparation of photocatalysts [54] and molecular machines [55]. Unlike the known multistep approaches which include the reduction of acridines to dihydroacridines followed by *N*-arylation [56, 57], this method gives access to this type of compounds in a single step.

New carbene-phosphine palladium complex **8b** can also efficiently catalyze the arylation of both primary and secondary amines under solvent-free conditions. The suggested method readily afforded different di- and triarylamines, including the unique derivatives of carbazole, dihydroacridine, and dithienopyrrole, in excellent yields.

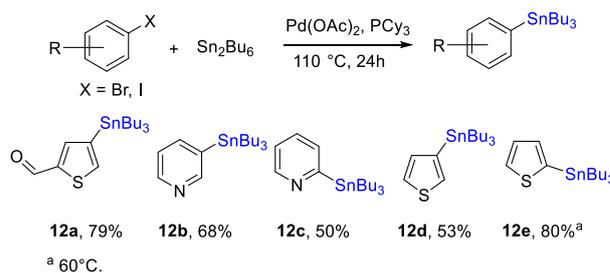
Solvent-free Stille reaction

The Stille reaction is among the most important methods for the synthesis of functionalized biaryls [58]. Owing to the high tolerance of arylstannanes towards different functional groups and their stability to air oxygen and moisture, nowadays, this reaction is widely used in the synthesis of highly functionalized bi(hetero)aryls [59–62]. The latter found extensive use as the components of optoelectronic devices and field transistors [63, 64] as well as the precursors for many pharmaceuticals [65–67] and pesticides [68].

Usually, the Stille cross-coupling is carried out using (hetero)aryltributylstannanes (Het)ArSnBu₃ as substrates, which are often commercially available and do not require preliminary synthesis from available precursors. A general method for the synthesis of different (Het)ArSnBu₃ is the palladium-catalyzed stannylation of (hetero)aryl halides using hexabutyldistannane (Sn_2Bu_6) [69]. However, it should be noted that the production and complicated purification of toxic arylstannanes as well as their following coupling with aryl halides make the synthesis of the target biaryls a complex multistep process that does not meet the requirements of environmental safety. Until recently, there

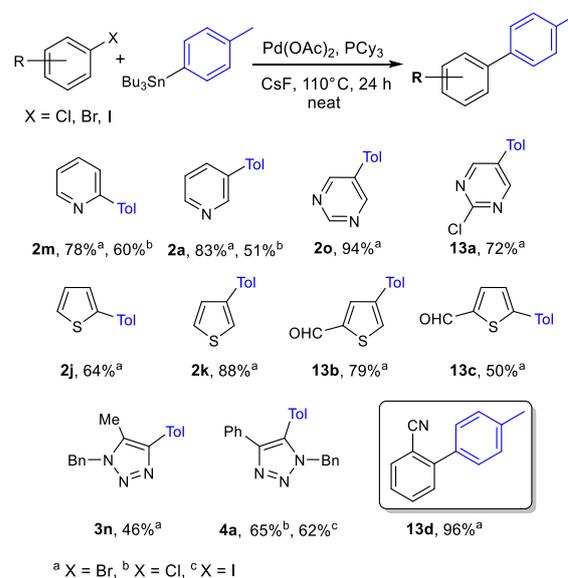
was only a single report [70] devoted to the development of the one-pot method for the synthesis of biaryls that implied the use of microwave activation under phase-transfer catalysis with high loadings of a palladium catalyst, a phase-transfer catalyst, and a base.

Recently, the new versatile conditions for the Stille reaction, which satisfy the modern requirements of ecological chemistry, have been suggested [71]. Based on the catalytic system $\text{Pd}(\text{OAc})_2/\text{PCy}_3$, an efficient and ecologically friendly method for the synthesis of different (hetero)arylstannanes under solvent-free conditions was developed. Besides the use in the Stille reaction, these (hetero)arylstannanes are convenient reagents for many chemical transformations (Scheme 11) [72–74].



Scheme 11. Synthesis of (hetero)arylstannanes.

The conditions selected for the stannylation of aryl halides were adapted further for the Stille cross-coupling (Scheme 12). The reactions can be performed using (hetero)aryl halides such as functionalized halogen-containing thiophenes, pyridines, and pyrimidines, resulting in the target cross-coupling products in good to excellent yields.



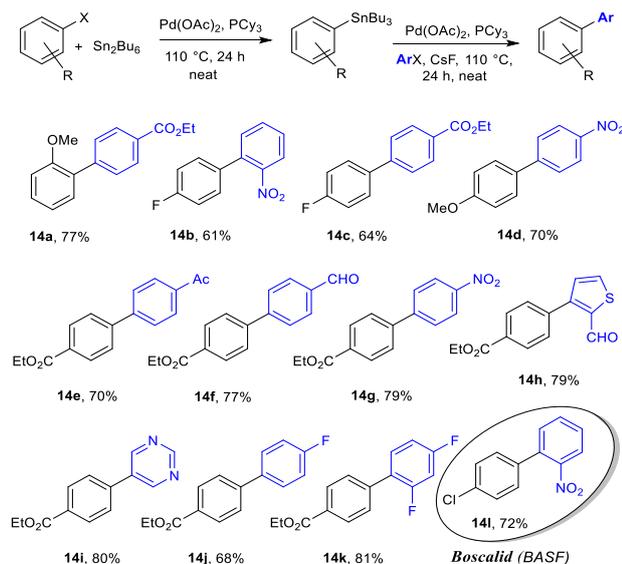
Scheme 12. Solvent-free Stille reaction.

The examples of syntheses of 1,2,3-triazole-containing products **3n** and **4a** demonstrated, for the first time, the principal possibility of the application of 5-halo-1,2,3-triazoles in the Stille reaction [30].

The results obtained testify the high degree of versatility and efficiency of the suggested methodology for the synthesis of

bi(hetero)aryl compounds of various natures that possess huge potential for practical application. Thus, cross-coupling product **13d** serves as a key intermediate in the production of the antihypertensive drugs Valsartan [65], Losartan [66], and Olmesartan [67] the most popular drugs for the treatment of hypertension.

The one-pot synthetic strategy to biaryls that essentially reduces the danger of contact with toxic organotin reagents was also suggested. The possibility of realization of this process firstly for the homocoupling of aryl halides and then for the synthesis of unsymmetrical biaryls was shown. The results obtained are presented in Scheme 13.



Scheme 13. One-pot stannylation–the Stille cross-coupling.

Both homocoupling [75] and cross-coupling [30, 71] are efficient reactions for a wide range of functionalized (hetero)aryl halides, independent from the nature and position of a substituent in the aromatic core. To show the possible practical application of the developed methodology, the synthesis of compound **14i** was accomplished, which serves as a key intermediate in the production of the pesticide Boscalid [68] produced by BASF (Germany) on a large scale since 2003. In general, the one-pot synthetic procedure is very simple and, in the case of the synthesis of unsymmetrical biaryls, implies sequential addition of a new portion of the same catalyst, a base, and the second aryl halide immediately after the completion of the stannylation step (monitoring by TLC).

A possibility of reaction scaling up and isolation of the target product from the reaction mixture by vacuum distillation was demonstrated [71]. The still residue bearing toxic tributyltin bromide and iodide before utilization is treated with a saturated solution of potassium fluoride to give the corresponding inert fluoride, which completely excludes the contact with toxic reagents.

The catalytic systems and conditions developed for the Suzuki–Miyaura, Buchwald–Hartwig, and Stille reactions, which do not imply the use of solvents, appeared to be highly efficient for a broad scope of different functionalized substrates. Compared to the conventional approaches, the suggested methodology offers the following advantages: (a) full absence of solvents and inert atmosphere; (b) low loadings of the

available catalysts and auxiliary reagents; (c) reaction activation by simple heating; (d) easy scaling up with no loss in the efficiency. All the developed cross-coupling protocols meet the modern requirements of green chemistry and can find application not only in laboratory practice but also in new environmentally benign industrial technologies.

4. Solvent-free copper-catalyzed reactions of acetylenes

Copper(I) NHC complexes in the synthesis of *N*-aryltriazoles

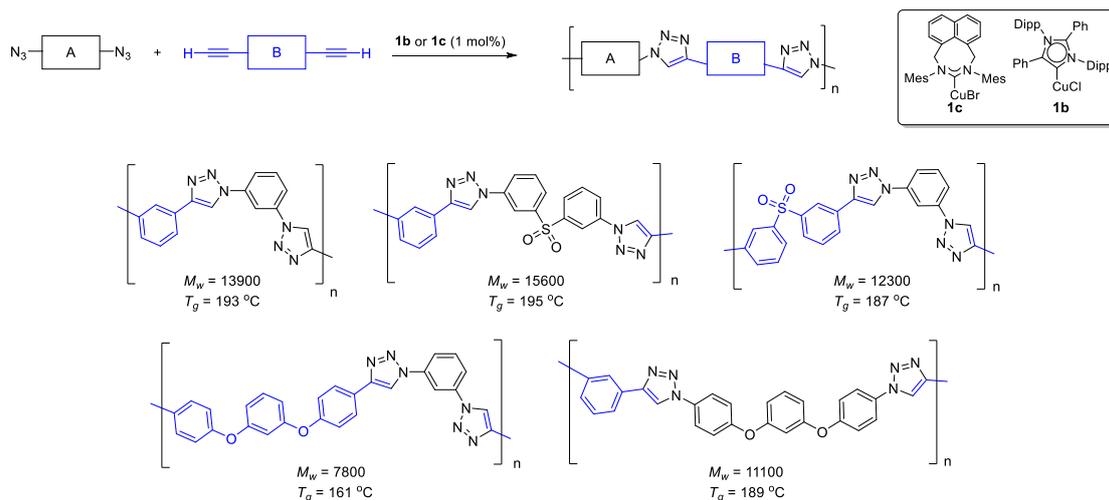
The successful application of transition metal complexes ($M = Pd, Au$) [37, 38, 76, 77] bearing *N*-heterocyclic carbenes with extended rings (*er*-NHC) as highly active catalysts for different C–C and C–N bond-forming reactions under solvent-free conditions promotes the investigations on the use of this strategy in Cu(I)-catalyzed cycloaddition (CuAAC) of acetylenes to low reactive aryl azides for the production of substituted aryltriazoles, which would significantly extend the number of catalytic methods and reactions that can be accomplished in accordance with the main principles of green chemistry.

Synthesis of poly(*N*-aryl-1,2,3-triazoles)

Nowadays, polymer composite materials play a key role in strategic industries such as space and aircraft engineering, automobile industry. Their application gives a significant economic effect and allows one to essentially reduce the construction mass and simultaneously exhibit high strength parameters. The use of polytriazoles as polymer matrices for the production of final items is considered to be especially promising since the polymers bearing aryltriazole units possess unique physicochemical properties. Their high thermal and chemical stability in a combination with a high propensity for self-organization into ordered supramolecular structures owing to the presence of conjugated aromatic bonds makes polytriazoles attractive research objects in the creation of innovative membrane and optoelectronic technologies, including the production of flexible solar cells. A distinctive feature of the technology for manufacturing polymer composites is the full absence of any solvent; therefore, the development of new synthetic approaches to polyaryltriazoles that would satisfy these requirements seems to be a very important area of modern fundamental and applied research.

The catalytic system for the click reaction of monoazides with monoacetylenes [78] was used to develop an efficient solvent-free method for the copolymerization of aromatic bis(azides) with aromatic bis(acetylenes) [79]. The monomer conversion and the amount of the resulting target polymers were controlled using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The molar masses of the products were determined by gel permeation chromatography (GPC). The comparable and high levels of catalytic activity were displayed by catalysts **1c** [78] and **1b** [80]. The target polytriazoles were obtained in almost quantitative yields (Scheme 14).

The preliminary evaluation of the properties of the resulting polymers showed that they possess excellent strength characteristics and thermal stability and can be successfully used



Scheme 14. Synthesis of polyaryltriazoles.

in the development of new composite materials by infusion of monomers followed by polymerization.

Synthesis of triazoles bearing azide and acetylene groups

In the last few years, the most promising direction in the chemistry of functionalized triazoles has been the development of selective methods for the synthesis of 1,2,3-triazole systems bearing reactive azide and/or acetylene groups. These compounds represent unique building blocks for the creation of whole libraries of bioactive compounds using combinatorial chemistry methods and the construction of complex triazole-containing supramolecular systems including macrocycles [81–86]. The presence of two and more triazole rings in these structures determines their great potential for practical application from ligands in transition metal catalysis to chemosensors and molecular machines.

The existing methods for the synthesis of acetylene/azide-containing triazoles [87, 88] are based on the orthogonality principle (different reactivities of the functional groups) which implies the manipulations with protecting groups [83, 89, 90], considerably complicating and extending a synthetic sequence.

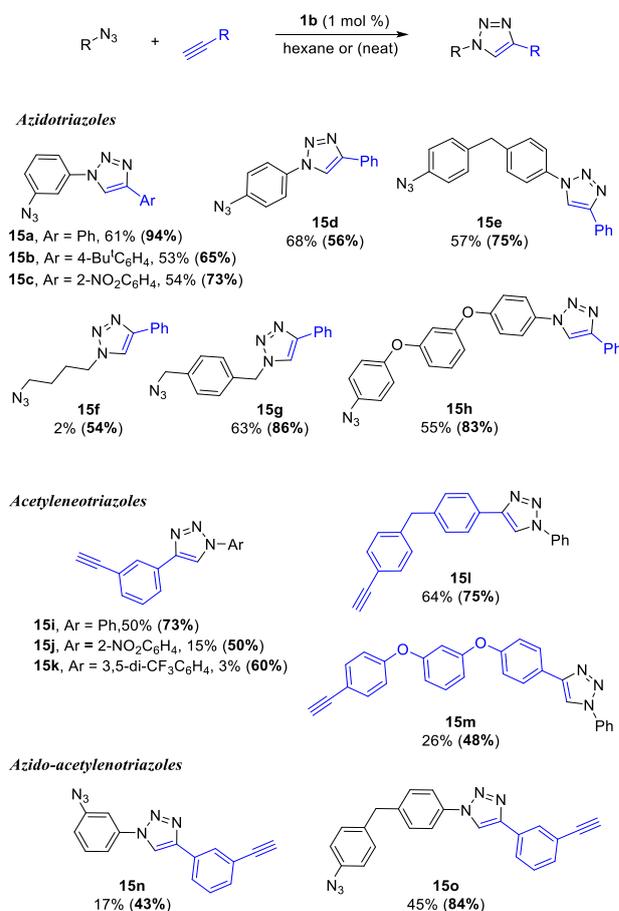
The click reaction involving a bis(azide) or bis(acetylene), bearing functional groups of comparable reactivities, usually leads to the formation of a statistical mixture of the initial reagents with mono- and dicycloaddition products. The developed approach [91] consists in the assurance of the mono-click reaction by the removal of a monofunctionalized product from a reaction medium using physical factors.

This issue was addressed by testing two possible ways of the termination of the first click reaction: 1) owing to the low solubility of the product which leads to its precipitation in a bad solvent and (2) owing to a significant increase in the medium viscosity under solvent-free conditions. Both the product precipitation and an increase in the medium viscosity can facilitate a decrease in the rate of side reactions.

Within the first approach, hexane was chosen as a solvent [92]. Unlike the initial acetylenes and organic azides, 1,2,3-triazoles are poorly soluble in hexane. The highest yields of the mono-click reaction products were achieved upon heating of a mixture of the equimolar amounts of the reagents in hexane (or

under solvent-free conditions) at 40 °C in the presence of 1 mol % of catalyst **1b** for 24 h (Scheme 15).

The results obtained suggest that both synthetic approaches (in hexane and in its absence) can be successfully realized for the synthesis of hardly accessible azido-, acetyleno- and azido-acetylenotriazoles from the corresponding symmetrical diazides and diacetylenes, and the former version is more preferential since affords the target products in high yields (Scheme 15).



Scheme 15. Synthesis of azido-, acetyleno- and azido-acetylenotriazoles (the bracketed values represent the compound yields in the absence of a solvent).

The observed selectivity is achieved owing to the removal from the reaction medium of the mono-click reaction product due to the effects of the concentration and antisolvent. The latter can be industrially important alkanes.

Application of *N*-aryltriazoles in the synthesis of phosphorescent iridium complexes

The methods developed for the synthesis of *N*-aryl-1,2,3-triazoles were tested for the solution of the applied problems using a series of phosphorescent iridium complexes [93]. Carbenes based on *N*-aryltriazoles were chosen as the key ligands that would be able to provide the required emission. It should be noted that nowadays trivalent iridium complexes are widely used as photosensitizers for photodynamic therapy of cancer [94, 95], sensors for oxygen and metal ions [96, 97], and components of organic light-emitting diodes (OLEDs [98, 99], light-emitting electrochemical cells (LEECs) [100, 101], *etc.*). A serious problem in the creation of OLEDs is the synthesis of phosphorescent compounds that would be able to emit in the blue spectrum region ($\lambda_{\text{max}} = 450\text{--}460\text{ nm}$) because blue OLEDs feature low service times due to the lower stability compared to green and red analogs. In this respect, particular attention of the researchers was drawn to *N*-heterocyclic carbene ligands able to shift the absorption band to the blue region of visible light.

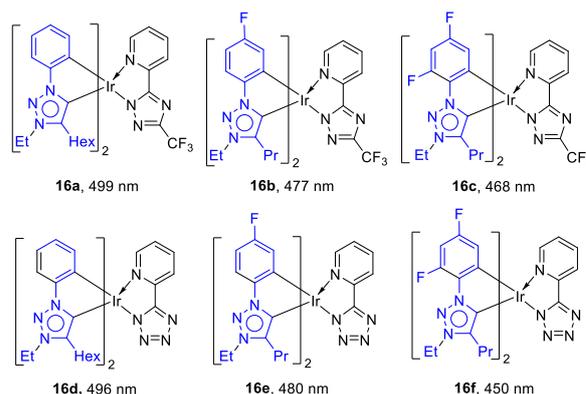
Recently, the directed synthesis of cyclometallated iridium complexes **16a–f** bearing 1,4-disubstituted 1*H*-1,2,3-triazol-5-ylidene ligands was accomplished and their photophysical properties were preliminarily studied (Scheme 16) [93]. It was revealed that the emission of this type of complexes depends on the nature and position of substituents in the cyclometallated aromatic core of the *N*-aryltriazole ligand. The availability of triazole ligands and the simplicity of their modification make these complexes a unique platform for rapid optimization of the photoluminescence properties *via* variation of substituents both in the aromatic and triazole moieties.

The emission characteristics of complexes **16c** and **16f** (Scheme 16) testify that the problem of synthesis of the emitters for blue OLEDs can be successfully solved using *N*-aryltriazole ligands.

5. Conclusions and future outlook

This highlight presented the efficient methodology for the most popular cross-couplings in modern synthetic chemistry, which lead to the selective formation of new carbon–carbon, carbon–nitrogen, and carbon–tin bonds, as well as heterocyclizations without recourse to organic solvents upon catalysis by available transition metal complexes bearing *N*-heterocyclic carbene or phosphine ligands.

The efficient method for the synthesis of diverse bi(hetero)aryl compounds by the Suzuki–Miyaura reaction in an aqueous medium enables the cross-coupling of (hetero)arylboronic acids with different heteroaryl halides, including low active heteroaryl chlorides (chloro-1,2,3-triazoles). The effective general solvent-free protocols devised for the first time for the most important metal-catalyzed reactions, in particular, the Suzuki–Miyaura, Stille, and Buchwald–Hartwig cross-couplings are described. The suggested conditions are applicable for a broad range of differ-



Scheme 16. Phosphorescent iridium complexes with cyclometallated triazole ligands.

ent functionalized aromatic substrates, independent from the electronic and steric properties of substituents. The versatile application of the specially developed catalytic system based on the mixed carbene-phosphine palladium complex is used for the efficient one-pot synthesis of di- and triarylamines, widely used in optoelectronics, from primary arylamines.

The principally new conditions for the click polymerization of aromatic bis(azides) with aromatic diacetylenes without the use of solvents open the way to new fields of application of aromatic polytriazoles in the creation of composite materials which hold great promise in aircraft and space industries. The developed synthetic approaches offer a unique opportunity for the directed synthesis of hardly available building blocks, such as multifunctional azido-, acetyleno- and azido-acetylenotriazoles required for the construction of new materials with the desired properties.

Besides obvious ecological and economic advantages, in some cases, the suggested conditions are not only comparable but even exceed the existing classical methods by the efficiency. Among the obvious advantages, of note are the full absence of solvents and inert atmosphere, low loadings of catalysts and auxiliaries, simple isolation of pure products, as well as a possibility of scaling up with no loss in the efficiency.

The described approaches are promising for the solution of the applied tasks in the priority fields of chemistry and technology including, for example, the following: 1) in the pharmaceutical industry, the production of highly pure precursors in the synthesis of drugs (Losartan, Boscalid) without metal impurities; 2) in the creation of new composite materials, the production of poly(*N*-aryl-1,2,3-triazoles); as well as 3) the design of new components for organic optoelectronics by the production of substituted arylamines, *N*-arylcarbazoles, and (1,2,3-triazol-5-ylidene)iridium complexes.

In conclusion, it should be noted that to date the field of solvent-free catalysis by transition metal complexes emerged from isolated examples to the individual methodology. The rejection of organic solvents makes many important catalytic processes highly selective, essentially simplifies the synthesis and purification procedures (reduces the number of stages) compared to the classical solution-based methods, and significantly minimizes the wastes polluting the environment. All this opens new prospects for the expansion of solvent-free methods and approaches to new classes of metal-catalyzed organic transformations.

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