TRANSITION-METAL-CATALYZED FUNCTIONALIZATION OF 1,10-PHENANTHROLINES AND THEIR COMPLEXES

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Abstract. *1,10-Phenanthroline is a classical ligand in coordination chemistry which is renowned among bidentate ligands for the generality of its stable metal complexes widely studied across many fields of chemistry, physics, biology and medicine. In this review we provide a detailed summary of experimental procedures which were developed to perform transition-metal-catalyzed reactions with halo-1,10-phenanthrolines. These data are discussed using selected examples showing how these reactions allow to expand beyond the range of available phenanthroline derivatives.*

Contents

1. Introduction

Metal complexes with nitrogen-containing ligands (porphyrins, polyazamacrocycles, bipyridines, phenanthrolines, dipyrromethenes and so forth) are widely studied across many fields of chemistry, physics, biology and medicine because their diverse and attractive structural, optical, magnetic, electrochemical and catalytic properties are promising for various analytical and technological applications. 1,10-Phenanthrolines (Phens) (Figure 1) are among most demanding N-ligands to develop supramolecular assemblies,[1-5] DNA intercalators and DNA-cleaving reagents,[6-8] sensors for cations, anions and other small molecules,[7,9-11] PDT agents,[12] redox catalysts,[13-17] photocatalysts[18-20] and photoactive electrodes for dye-sensitized solar cells.[21] Due to a strong electronic interaction of the Phen ligand and metal centers, the physical and chemical properties of metal complexes can be tuned varying the substitution pattern of the heteroaromatic scaffold. Therefore, the development of synthetic approaches to Phen chelators bearing different substituents at the

heterocycle periphery or covalently bonded to other functional sites promotes forward studies in many research fields.

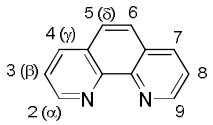


Figure 1. Numeration of the positions in 1,10-phenanthroline.

For a long time, Phens were mainly prepared by multistep syntheses from aniline and quinoline precursors.[22] More recently, post-synthetic modifications of the heteroaromatic scaffold were recognized as powerful strategies for Phen functionalizations.[7] Many of these syntheses involve chemical transformations of halogenated Phen derivatives using carbon–carbon and carbon–heteroatom (N, P, B) bond forming reactions. 2- And 4-halo-substituted Phens are activated for nucleophilic substitution reactions and react easily with oxygen, nitrogen or sulfur nucleophiles. By contrast, the nucleophilic substitution of halogens located at positions 3 and 5 of the Phen core demands the application of transition metal (TM) catalysis. Symmetrical dihalophenanthrolines can also be obtained in good yields and transformed into corresponding difunctionalized derivatives. Moreover, sometimes the nucleophilic substitution of one or the two halogen atoms at the heterocyclic ring can be performed selectively, thus allowing for the synthesis of unsymmetrically substituted derivatives.

Taking profit of these nucleophilic substitution reactions, the substituents can be introduced at all positions (at α, β, γ and δ positions relative to the nitrogen atom, Figure 1) of conjugated aromatic rings which allows systematic tuning of electronic and steric properties of these bidentate chelators. Therefore, one can obtained Phen chelators containing both electron donor and electron deficient substituents, molecular architectures possessing expanded conjugated systems, dyads in which Phen residue is combined with porphyrins or another chromophore and even more sophisticated molecular systems displaying a programmed arrangement of donor sites required in supramolecular chemistry and polymer science.[7]

Among these substitution reactions, TM-mediated reactions are the most difficult to perform due to a low solubility of starting halides and a strong metal chelating ability of Phens. In this review, we critically evaluate experimental procedures which were developed to overcome these difficulties. These data are discussed using selected examples showing how these reactions allow to expand beyond the range of available Phen derivatives. The synthesis of halo-substituted 1,10-phenanthrolines from commercially available compounds is also briefly reviewed as these are essential intermediate compounds in the synthesis of Phens through TM-catalyzed reactions.

2. Synthesis of halophenanthrolines

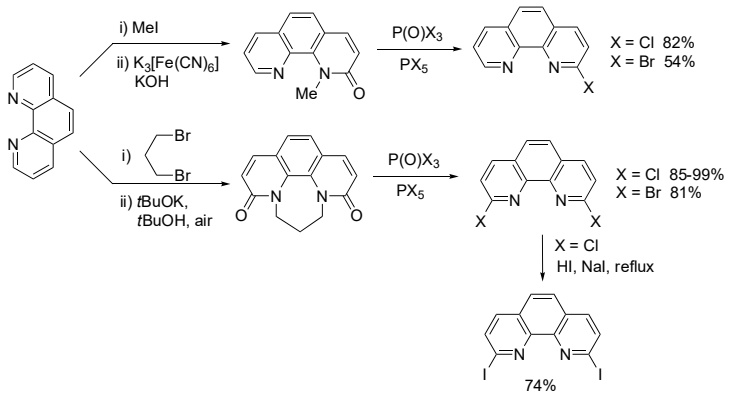
Most of TM-catalyzed reactions suitable for Phen synthesis involve mono- and dihalo-substituted derivatives as intermediate compounds. Synthetic approaches to these halides are specific for each isomer. Since bromides are suitable substrates for most catalytic transformations of Phens, the synthesis of corresponding iodides (commonly more expensive relative to bromides) is less explored.

Particular feature of Phen halides compared to aryl counterparts is the high reactivity of chlorine located at α and γ positions of the Phen core because of the electronegative nitrogen in the peripheral aromatic rings. Moreover, chlorides can be obtained using less expensive reagents and in higher yields than corresponding bromides. Therefore, they are commonly used as starting compounds to perform functionalization of α and γ positions of the Phen core.

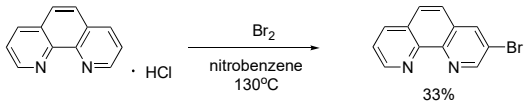
2-Chloro- and 2-bromo-substituted 1,10-phenanthrolines are prepared from Phen through the oxidation to 1-methyl-1,10-phenantrolin-4(1*H*)-one followed by its reaction with phosphoryl halides (Scheme 1).[23] The analogous three-step approach to 2,9-dicloro- and 2,9-dibromo-1,10-phenanthrolines was described.[24,25] Corresponding diiodide was prepared in 74% yield from 2,9-dichloro-l,10-phenanthroline by the nucleophilic substitution of chlorine atoms (Scheme 1).[26]

To carry out the functionalization of Phen scaffold at β positions, corresponding bromides are most suitable intermediate compounds. 3-Bromo-1,10-phenanthroline can be obtained in 33% yield by the

bromination of Phen hydrochloride in nitrobenzene at 130 °C using substoichiometric amount of bromine (Scheme 2).[27] Though this method allows the recovery of the unreacted Phen, it is rather tedious due to inevitable separation of the product from side 3,8- and 3,6-dibromo-1,10-phenanthrolines by column chromatography.

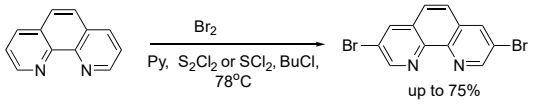


Scheme 1. Synthesis of 2-halo- and 2,9-dihalo-1,10-phenanthrolines.



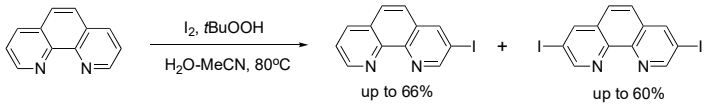
Scheme 2. Synthesis of 3-bromo-1,10-phenanthroline.

3,8-Dibromo-1,10-phenanthroline was synthesized by the bromination of Phen in 1-chlorobutane in the presence of pyridine and sulfur monochloride (Scheme 3).[28,29] The product has been subjected to a tedious column chromatography to separate side dibromides and sulfur-containing by-products which could affect the following catalytic reactions. When sulfur monocloride was replaced by sulfur dichloride, the dibromide was obtained in low yield (14%).[30] However, using this catalyst, 3,5,8-tribromo- and 3,5,6,8-tetrabromophenantrolines can be prepared in 11-19% yields after increasing the bromine amount up to 4.8 equivalents.[30]



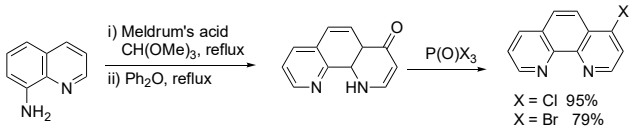
Scheme 3. Synthesis of 3,8-dibromo-1,10-phenanthroline.

Quite recently, 3-iodo-phenanthroline was obtained in good yield by reacting Phen with iodine in the presence of *tert*-butyl hydroperoxide (Scheme 4).[31] Very similar conditions were employed for the preparation of 3,8-diiodo-1,10-phenanthroline, but the experimental procedure was not detailed (Scheme 4).[32] These compounds exhibit excellent reactivity in the cross-coupling reactions and may serve as an attractive alternative to above mentioned bromo derivatives.



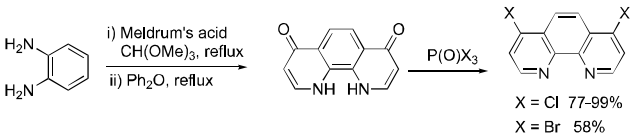
Scheme 4. Synthesis of 3-iodo- and 3,8-diiodo-1,10-phenanthrolines.

4-Chloro- and 4-bromo-1,10-phenanthrolines are available from 8-aminoquinoline (Scheme 5).[33,14] The quinoline is initially treated with Meldrum's acid in trimethyl orthoformate to obtain an adduct that cyclizes in refluxing diphenyl ether to give 4-hydroxyphenanthroline. Successive treatment of 4-hydroxyphenanthroline with phosphoryl chloride or bromide affords the chloro- or bromo-substituted Phens, respectively.



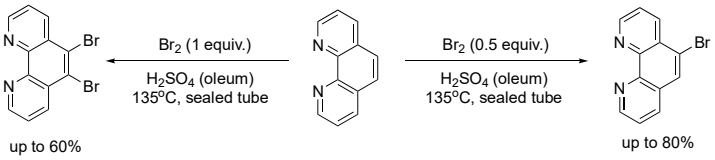
Scheme 5. Synthesis of 4-halo-1,10-phenanthrolines.

4,7-Dihalo-1,10-phenanthrolines were synthesized in good yields by the same procedure from *ortho*-phenylenediamine (Scheme 6).[34]



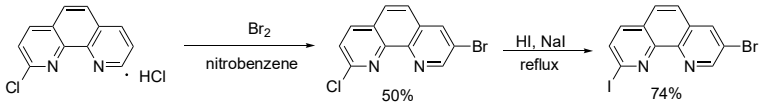
Scheme 6. Synthesis of 4,7-dihalo-1,10-phenanthrolines.

To functionalize Phens at δ positions, the most suitable starting compounds are 5-bromo- and 5,6-dibromo-1,10-phenanthrolines. They can be prepared by the bromination of Phen in oleum in a sealed vessel at 135 °C (Scheme 7).[35-37] The formation of the mono- or dibromo-substituted compound is ensured by using of 0.5 or 1 equiv. of bromine, respectively.



Scheme 7. Synthesis of 5-bromo- and 5,6-dibromo-1,10-phenanthrolines.

Several synthetic approaches to unsymmetrically substituted di- and tribromides have been reported.[26,30,38,39] Many of them give the target products in low yields and after laborious chromatographic separations. However, the reaction of 2-chloro-l,10-phenanthroline hydrochloride with bromine in nitrobenzene affords 8-bromo-2-chloro-l,10-phenanthroline in 50% yield after chromatography; some starting material is recovered and can be recycled (Scheme 8).[26] The chloride can be replaced by iodide to give 8-bromo-2-iodo-1,10-phenanthroline in 74% yield.



Scheme 8. Synthetic approach to 2-chloro- and 2-iodo-substituted 3-bromo-1,10-phenanthrolines.

3,5,6,8-Tetrabromophenanthroline was prepared in 52% yield after recrystallization of a crude product obtained by reacting Phen with bromine in the presence of thionyl chloride (Scheme 9).

Nowadays, many of these halophenanthrolines are commercially available at a reasonable price, which facilitates the realization of the TM-catalyzed reactions reviewed below.

Scheme 9. Synthesis of 3,5,6,8-tetrabromophenanthroline.

3. Transition-metal-catalyzed functionalization of Phens

3.1. C–C coupling

C–C bond formation plays a central role in the organic synthesis. It is no wonder, therefore, that TM-catalyzed C–C bond forming reactions for the modification of the Phen backbone have been widely explored. Several alternative routes are often available to prepare a target ligand that is particularly important in chemical transformations of low soluble halo-1,10-phenanthrolines and in the synthesis of Phens bearing reactive functional groups and residues.

3.1.1. Sonogashira cross-coupling

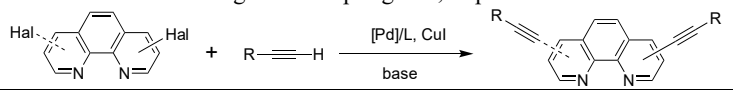
Preparation of ethynyl-substituted Phens through the Sonogashira reaction was reported by Suffert and Zeissel[40,41] and seems to be the first Pd-catalyzed process in which halo-substituted Phens were involved as substrates. The acetylene residue allows for extension of the Phen aromatic system and could provide covalent bonding of the Phen moiety with other functional elements ensuring the overall molecular rigidity and π-conjugation. Acetylenic linkers are widely used for the preparation of covalently linked multi-chromophore arrays, compounds for molecular electronics and macrocyclic structures.

Sonogashira coupling is widely applied to the synthesis of ethynyl-substituted Phens due to its easy accomplishment and weak dependence on the nature of the substituents in alkynes. There are over hundred examples of successful coupling of Phens with various alkyne substrates reported in literature. Representative transformations with phenylacetylene and trimethylsilylacetylene are summarized in Table 1. The reactions are smoothly run using classical catalytic systems like $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ in the presence of CuI co-catalyst. The catalyst loading is usually 5-10 mol%, though there are examples of successful coupling after decreasing the catalyst amount to 1-3 mol% (entries 7, 8, 15 and 16). That 1,10-phenanthroline can bind copper ions obviously does not hamper the reaction but additional treatment sometimes is needed to isolate the product in good yield.[40] Diisopropylamine or triethylamine are typically used as bases and are taken in great excess probably to compete with 1,10-phenanthroline in copper binding. 2- And 4-substituted phenanthrolines can be synthesized from both chloro- or bromo-substituted Phens (entries 5 and 14), while for 3- and 5-isomers, bromides are preferable starting compounds due to a lower reactivity of corresponding chlorinated Phens (entry 1 and 9). For example, the reaction with 5-chloro-1,10-phenanthroline with phenylacetylene provides a low (16%) yield of the product (entry 3) while the bromide affords the same product in 60% yield. Moreover, the reaction of the bromide with trimethylsilylacetylene can be performed at room temperature (entry 1), though in the most cases the coupling reactions are conducted on heating.

Disubstituted Phens can be obtained through Sonogashira reaction using dihalo-Phens as starting compounds. All symmetrical isomeric 2,9, 3,8 and 4,7 derivatives were obtained in high yields (entries 7, 8, 11, 12, 13, 16 and 17). When 3,8-diiodo- and 3,8-dibromo-1,10-phenanthrolines were reacted with phenylacetylene, the target product was isolated in comparable yields (76 and 82%, respectively; entries 12 and 13). The scope of alkyne precursors is very large and some representative examples are summarized in Table 1 (entries 4, 6, 10 and 17). The copper-free Sonogashira reaction was also reported by several groups (entries 6,10 and 13). The products of the reaction with trimethylsilylacetylene after the removal of the protecting Me_3Si group can be further introduced in the Sonogashira reaction or in the copper(I)-catalyzed azide alkyne cycloaddition reaction (CuAAC).

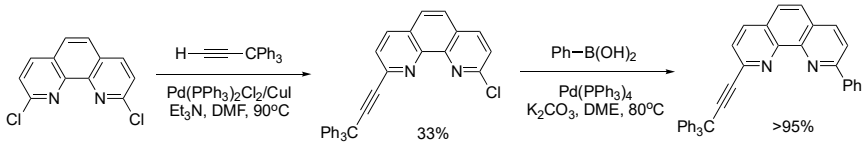
In less reactive dichlorides, substitution of one of two chlorine atoms was shown to be possible,[42] though the yield was modest (Scheme 10) due to competing substitution of the second halogen atom. The target product was further introduced in the Suzuki coupling to give unsymmetrically substituted 1,10-phenanthrolines.

Table 1. Sonogashira coupling of 1,10-phenanthrolines.



Entry	Position(s)	Hal	R	Catalyst (mol%)	Reaction conditions	Yield, (%)	Ref.
1	5	Br	TMS	$PdCl_2(PPh_3)_2$ (10),CuI (11)	iPr_2NH, THF, rt, 24 h	85	[43]
2	5	Br	Ph	$Pd(PPh_3)_4$ (10), CuI (10)	iPr_2NH, THF, 80 °C, 48 h	60	[44]
3	5	Cl	Ph	$PdCl_2(PPh_3)_2$ (15),CuI (34)	Et_3N, DMF, 90 °C, 8 h	16	[45]
4	5,6	Br	pyren-1-yl	$Pd(PPh_3)_4$ (10), CuI (10)	iPr_2NH, benzene, 60 °C	75	[46]
5	4	Br	Ph	$PdCl_2(DPPF)^a$ (10), CuI (10)	Et_3N, DMF, rt	65	[47]
6	4	Cl	2,2':5',2''-terthien-3'-yl	$Pd(PPh_3)_4$ (10)	Et_3N, H_2O-dioxane, reflux, 48 h	90	[48]
7	4,7	Br	Ph	$PdCl_2(PPh_3)_2$ (3), CuI (4)	Et_3N, DMF, 90 °C, 18 h	95	[49]
8	4,7	Cl	Ph	$PdCl_2(PPh_3)_2$ (2), CuI (7)	Et_3N, DMF, 90 °C, 8 h	87	[45]
9	3	Br	TMS	$PdCl_2(PPh_3)_2$ (5), CuI (10)	Et_3N, benzene, 80 °C, 72 h	92	[50]
10	3	Br	pyren-1-yl	$Pd(PPh_3)_4$ (15)	$PrNH_2$, 80 °C, 48 h	79	[37]
11	3,8	Br	TMS	$PdCl_2(PPh_3)_2$ (5), CuI (10)	Et_3N, DMF, 80 °C, 72 h	88	[51]
12	3,8	Br	Ph	$PdCl_2(PPh_3)_2$ (10), CuI (11)	iPr_2NH, DMF, reflux, 4 h	82	[52]
13	3,8	I	Ph	$Pd(PPh_3)_4$	$PrNH_2$, reflux, 48 h	76	[32]
14	2	Cl	TMS	$PdCl_2(PPh_3)_2$ (10), CuI (10)	Et_3N, DMF, 60 °C, 12 h	60[b]	[53]
15	2,9	Cl	TMS	$PdCl_2(PPh_3)_2$ (1.5), CuI (3)	Et_3N, DMF, 90 °C, 18 h	63	[54]
16	2,9	Cl	Ph	$PdCl_2(PPh_3)_2$ (2), CuI (4)	Et_3N, DMF, 90 °C, 18 h	89	[54]
17	2,9	I	2-amino-5-(*t*-butyl)phenyl	$Pd(PPh_3)_4$ (10), CuI (110)	iPr_2NH, THF, rt, 24 h	74	[55]

[a]DPPF=1,1′-bis(diphenylphosphino)ferrocene.
[b]The yield of deprotected product (R=H) obtained after hydrolysis of TMS group.



Scheme 10. Stepwise catalytic difunctionalization of 2,9-dichloro-1,10-phenanthroline.

3.1.2. Suzuki-Miyaura cross-coupling

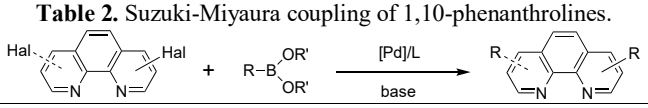
The Suzuki-Miyaura reaction was first applied to Phen derivatives by Chan's group,[56] and has become one of the most frequently used cross-coupling reactions for the preparation of functionalized Phens including polydentate chelators widely investigated in coordination and supramolecular chemistry. The introduction of aromatic and heteroaromatic fragments at different positions of the phenanthroline scaffold allows fine tuning not only of its electron and steric properties but also of the number and nature of external coordination sites of the ligand. Representative reactions are summarized in Table 2.

High yields of the coupling products were obtained employing air-sensitive $Pd(PPh_3)_4$ as a catalyst (entries 1, 4, 5, 7-15 and 18) but $PdCl_2(PPh_3)_2$ (entry 3) and $PdCl_2(DPPF)$ (entries 16 and 17) work also well in this reaction. Moreover, the catalyst can be prepared *in situ* from $Pd_2(dba)_3$ and bulky phosphine ligands (entries 2, 6 and 20). Sodium or potassium carbonates are common bases but sometimes potassium acetate can afford the product in higher yield.[57] Water in small amounts is also generally required, probably to form a more reactive Phen monohydrate and to accelerate the transmetalation step of the catalytic cycle. The reaction is generally conducted using 5-10 mol% of catalyst on heating under inert atmosphere. 2,9-Dichloro- and 4,7-dichloro-1,10-phenanthrolines are as active as corresponding bromides, and the scope of aryl- and heteroarylboronic acids or their esters suitable for this reaction is very wide. Nevertheless, it is worth noting that 2,9-disubstituted derivatives can be obtained much more easily by the direct Sauvage arylation of Phen.[58]

Coupling of dihalides can be performed regioselectively *via* the substitution of only one of two halogen atoms by varying the nature and position of halogen atoms in the aromatic scaffold. Iodine is the most active at the oxidative addition step of the catalytic cycle, in particular being located at α and γ

positions of the pyridine rings. Accordingly, coupling of 8-bromo-2-iodo-1,10-phenanthroline with an equimolar amount of 4-methoxyphenylborobic acid proceeds regioselectively at the α position affording the product bearing unreacted bromine atom (Scheme 11).[26]

Table 2. Suzuki-Miyaura coupling of 1,10-phenanthrolines.



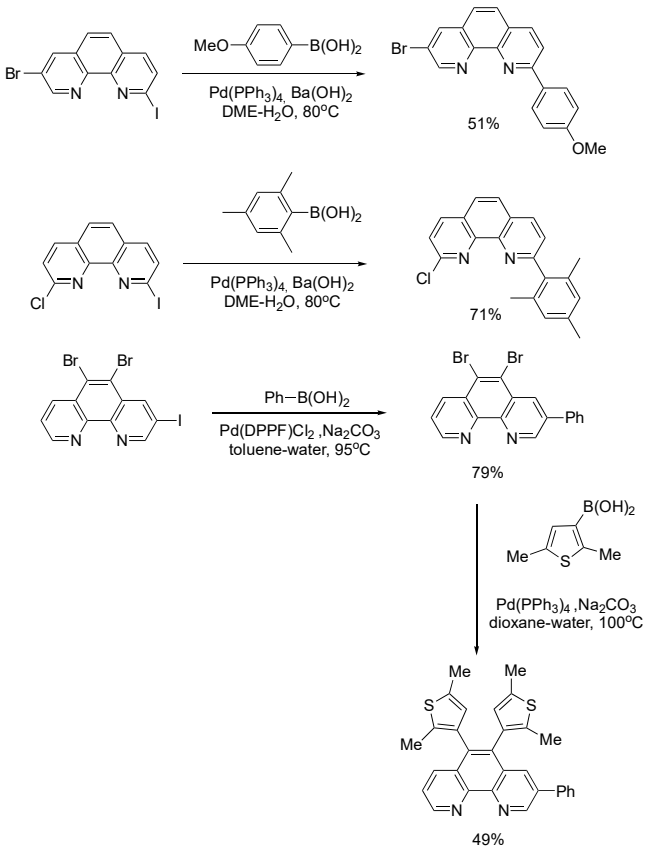
Entry	Position(s)	Hal	R	Catalyst [Pd]/L	Reaction conditions	Yield, (%)	Ref.
1	5	Br	pyren-1-yl	$Pd(PPh_3)_4$	$Ba(OH)_2$, H_2O-EtOH-toluene, reflux, 48 h	63	[60]
2	5	Br	4-(Ph_2N)-Ph	$Pd_2(dba)_3$/tBu_3P	Na_2CO_3, H_2O-PrOH-toluene, reflux, 48 h	77	[61]
3	5	Br	2,2':6',2"-terpyridin-4'-yl	$PdCl_2(PPh_3)_2$	K_2CO_3, DMSO, 100 °C, 24 h	73	[62]
4	5,6	Br	2,5-dimethylthiophen-3-yl	$Pd(PPh_3)_4$	Na_2CO_3, H_2O-THF, reflux	44	[63]
5	3,5,6,8	Br	Ph	«	Na_2CO_3, H_2O-toluene, reflux	71	[64]
6	4,7	Cl	4-*t*Bu-Ph	$Pd_2(dba)_3$/PCy_3	Cs_2CO_3, H_2O-dioxane, 100 °C, 3 h	84	[65]
7[a]	4,7	Cl	Ph	$Pd(PPh_3)_4$	K_2CO_3, H_2O-THF, reflux	98	[66]
8[b]	4,7	Br	4-pyridyl	«	K_2CO_3, H_2O-dioxane, 130 °C, 2 h	82	[67]
9	3	I	Ph	«	K_2CO_3, H_2O-toluene, reflux, 24 h	76	[68]
10	3,8	I	Ph	«	K_2CO_3, H_2O-toluene, reflux, 24 h	90	[68]
11	3	Br	4-MeO-Ph	«	Na_2CO_3, H_2O-EtOH-toluene, reflux, 24 h	90	[69]
12	3	Br	thiophen-3-yl	«	Na_2CO_3, EtOH-toluene, 80 °C, 12 h	85	[70]
13	3,8	Br	Ph	«	Na_2CO_3, H_2O-THF-toluene, reflux, 18 h	81	[71]
14	2	Br	thiophen-2-yl	«	Cs_2CO_3, H_2O-dioxane, reflux, 8 h	87	[72]
15	2	Cl	4-	«	Cs_2CO_3, DME, 80 °C, 6 h	62	[73]
16[c]	2	Cl	4-$(EtO)_2P(O)$Ph	$PdCl_2$(DPPF)[d]	Cs_2CO_3, dioxane, reflux, 3 h	70	[74]
17	2,9	Cl	Ph	«	$Ba(OH)_2$, H_2O-toluene, 110 °C, 6 h	90	[75]
18	2,9	Cl	4-pyridyl	$Pd(PPh_3)_4$	Na_2CO_3, H_2O-DME, reflux, 20 h	84	[76]
19	2,9	Cl	2,6-diMeO-Ph	«	Na_2CO_3, H_2O-DME, reflux, 20 h	83	[77]
20	2,9	Cl	3-methyl-1H-indol-7-yl	$Pd_2(dba)_3$/SPhos[e]	K_3PO_4, H_2O-toluene, 90 °C, 48 h	54	[78]

[a]4,7-Dibromo-2,9-dimethyl-1,10-phenanthroline was used. [b]4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline was used.
[c]2-Chloro-9-(4-methoxyphenyl)-1,10-phenanthroline was used. [d]DPPF=1,1′-bis(diphenylphosphino)ferrocene.
[e]SPhos=2-(dicyclohexylphosphino)-2′,6′-dimethoxybiphenyl.

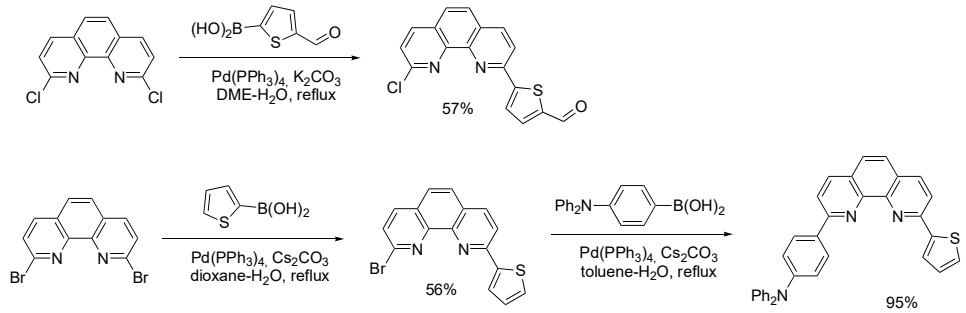
The Suzuki-Miyaura reaction of 2-chloro-9-iodo-1,10-phenanthroline also can be performed selectively at the α position if the amount of boronic acid is controlled (Scheme 11).[26] Another example of the regioselective substitution is the coupling of 5,6-dibromo-3-iodo-1,10-phenanthroline with phenylboronic acid (Scheme 11). These regioselective reactions can be followed by the second coupling with a boronic acid to give unsymmetrical Phens, as shown in Scheme 11 for 5,6-dibromo-3-iodo-1,10-phenanthroline.[59] At the first step $PdCl_2$(DPPF) complex was employed as a catalyst while $Pd(PPh_3)_4$ was used at second step. However, the authors did not provide an explanation for such change of the catalyst.

Regioselective substitution of only one of two identical halogen atoms in dihalophenanthrolines was also reported. For example, 2,9-dihalo-1,10-phenanthrolines react with thienylboronic acids affording mono-thienyl-substituted Phens which are convenient intermediate compounds to prepare Phens bearing two different aromatic substituents (Scheme 12).[73,79]

Phen derivatives can also be synthesized *via* the Suzuki-Miyaura reaction using phenanthrolinylboronic esters which can be available from halo-substituted Phen through a Miyaura-Ishiyama borylation reaction. This approach is particularly attractive when homo-coupled side products are difficult to separate by column chromatography as in the case of ditopic ligand combining 2,9-dimethyl-1,10-phenanthroline and terpyridine structural units (Scheme 13).[57]



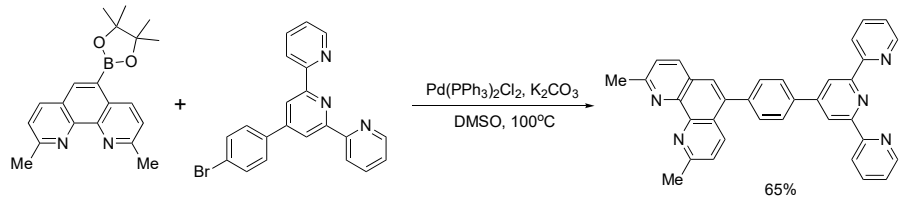
Scheme 11. Regioselective Pd-catalyzed Suzuki-Miyaura reaction of iodo-substituted Phens.



Scheme 12. Regioselective Suzuki-Miyaura reactions of 2,9-dihalo-1,10-phenanthrolines and an example of their use for preparation of unsymmetrical Phens.

3.1.3. Stille cross-coupling

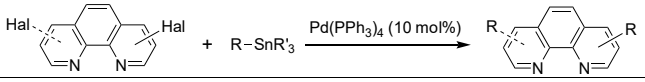
The Stille reaction is an alternative to the Suzuki coupling in the synthesis of biaryls which are widely used in the organic synthesis, but not very common in the Phen chemistry likely due to a strong ligation of these chelates to tin(IV) organometallics.[80,81] Nevertheless, this reaction also was employed for the introduction of the substituents at all carbon atoms of the phenanthroline core.



Scheme 13. Suzuki-Myaura coupling of phenanthrolinylboronic ester and an aryl halide.

As shown in Table 3 (entries 2, 4-6 and 9), this reaction proceeds in the presence of palladium(0) complexes with triphenylphosphine and is convenient for the preparation of heteroaryl-substituted phenanthrolines. For example, the introduction of thiophenyl residues (entries 2 and 4) attracted considerable interest as the corresponding starting compounds are available and the products are required for the construction of organic electronic materials. The Stille reaction seems to be the best pathway to vinyl-substituted Phen (entries 6 and 7) as the Mizoroki-Heck reaction in Phen series was rarely used (see below).[82,83]

Table 3. Stille coupling of 1,10-phenanthrolines.



Entry	Position(s)	Hal	R'	R	Reaction conditions	Yield, (%)	Ref.
1	5,6	Br	Me	5-methylthiophen-2-yl	DMF, 85 °C, 65 h	81	84
2	4,7	Br	Bu	5,5"-dialkyl-2,2':3',2"-terthien-5'-yl	DMF, 110 °C, 65 h	85	85
3	3,8	Br	Me	4-octylthiophen-2-yl	DMF, 120 °C, 3 d	36	86
4[a]	3,8	Br	*n*Bu	2,3-dihydrothieno[3,2-b][1,4]diox-in-6-yl	THF-DMF, 130 °C, 15 h	53	87
5	2	Br	*n*Bu	2-pyridyl	toluene, reflux, 4 d	89	88
6	2	Br	*n*Bu	6-bromopyridine-2-yl	toluene, reflux, 5 d	90	88
7	2,9	Cl	*n*Bu	vinyl	toluene, 110 °C, 7 h	22	83
8[b]	2,9	Cl	*n*Bu	1-ethoxyvinyl	DMF, 80 °C, 60 h	69	82
9	2,9	Cl	*n*Bu	2-pyridyl	toluene, reflux, 3 d	89	89

[a]The catalyst was obtained by reduction of $PdCl_2(PPh_3)_2$ with BuLi in THF. [b]$PdCl_2(PPh_3)_2$ was used as a catalyst.

3.1.4. Negishi cross-coupling

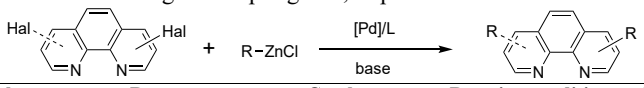
The Negishi coupling is also not so widespread for the Phen functionalization as the Suzuki-Miyaura reaction probably due to the formation of stable and insoluble zinc complexes with Phen which were isolated and characterized by single crystal X-ray analysis.[90] In some cases, however, purification of zinc complexes obtained in the Negishi reaction is simpler compared to the isolation of corresponding Phen ligands. These complexes are particularly useful in the preparation of polydentate ligands which are difficult otherwise to purify by column chromatography.[33,91] Thus, an important condition of successful proceeding of the Negishi coupling seems to be the engagement of zinc dichloride in excess.

Reported examples demonstrate that the Negishi coupling being run in THF allows the introduction of aromatic and heteroaromatic residues at all carbon atoms of the Phen scaffold using bromo- and iodo-substituted Phens as starting compounds (Table 4, entries 1, 2, 4 and 8). Steric hindrance of organozinc compounds does not affect the reaction outcome. However, the product yields can be quite low as it was observed in the reactions of 4- and 5-bromo-1,10-phenantrolines with electron rich aryl zinc derivatives (entries 1 and 2). Di- and tetra-substitution reactions proceed smoothly affording the target product in high yields (entries 3-7, 9 and 10). Moreover $C(sp^2)$–$C(sp^3)$ and $C(sp^2)$–C(sp) bond formation can be achieved using organozinc compounds (entries 6 and 7, respectively).

The Negishi reaction with dihalophenanthrolines can be performed regioselectively to form mono-substituted products. These intermediate compounds can be introduced in the Negishi or other cross-coupling reactions to form unsymmetrical derivatives, in particular pyridylphenanthroline derivatives (Scheme 14).[33,91] However, the reaction yields are highly dependent on the structure of starting Phens. For

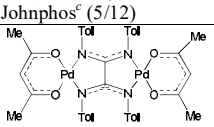
example, the substitution of the α-iodine in 2,9-diiodo- and 8-bromo-2-iodo-1,10-phenanthrolines proceeds in good yields. In the case of 2,7-dibromo-1,10-phenanthroline in which both bromo substituents are activated to the substitution being located in α and γ positions of the pyridine ring, the selectivity was not achieved; a mixture of 2- and 7-substituted products was obtained, and the product of α substitution was isolated in only 18% yield. Further synthetic modification using the Negishi coupling was also possible only in selected cases due to a low solubility of Zn complexes of the intermediate compounds. The Suzuki-Miyaura coupling can be employed to overcome this drawback as shown in Scheme 14.

Table 4. Negishi coupling of 1,10-phenanthrolines.

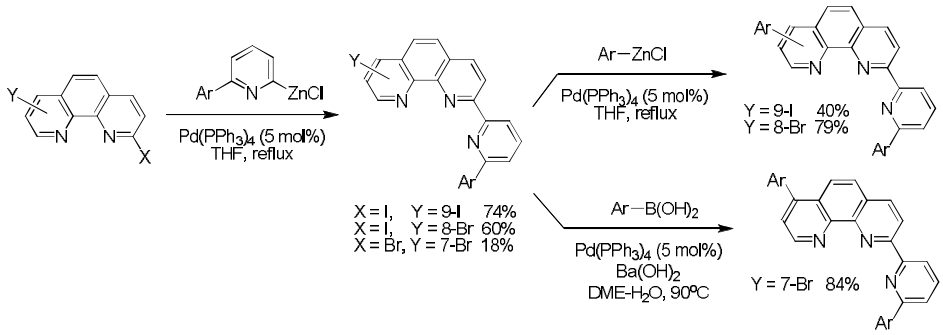


Entry	Position(s)	Hal	R	Catalyst [Pd]/L (mol%)	Reaction conditions	Yield, (%)	Ref.
1	5	Br	4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)phenyl	$Pd(PPh_3)_4$ (5)	THF, rt, 3 h	18	92
2	4	Br	2,6-dimethyl-4-methoxy-phenyl	$Pd(PPh_3)_4$ (10)	THF, reflux, 15 h	15	91
3	4,7	Br	4-CF_3-phenyl	«	THF, reflux, 12 h	59	93
4	3,8	Br	mesityl	$Pd(PPh_3)_4$ (1)	THF-toluene (C_{Phen}= 0.08 M), 120 °C, 17 h	71	94
5	3,8	Br	2,2'-bithiophen-5-yl	$Pd(OAc)_2/PPh_3$(10/20)	THF, 70 °C, 19 h	75	95
6	3,8	Br	$CH_2Si(Me)_3$	$Pd(PPh_3)_4$ (4)	THF-toluene, 100 °C, 3 h	64[a]	96
7	3,5,6,8	Br	phenylethynyl	CAT[b] (20)	THF, 150 °C, 7 h	60	90
8	2	I	2,6-dimethyl-4-methoxyphenyl	$Pd(PPh_3)_4$ (10)	THF, reflux, 15 h	69	91
	3	Br					
9	2,9	I	2-tiophenyl	«	THF, rt, 24 h	92	97
10	2,9	I	pentafluorophenyl	$Pd(OAc)_2$/Cy-Johnphos[c] (5/12)	THF, 90 °C	65	98

[a]The product yield obtained after hydrolysis. [b]CAT=



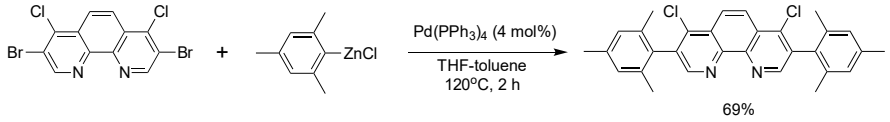
[c]CyJohnphos=2-(dicyclohexylphosphino)biphenyl.



Scheme 14. Stepwise difunctionalization of dihalo-1,10-phenanthrolines *via* the Negishi reaction followed by the second coupling reaction.

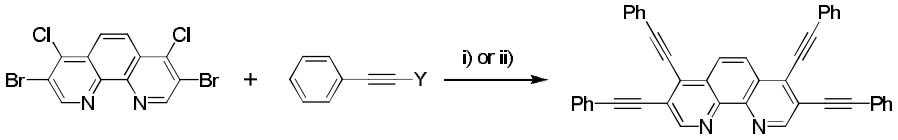
Further increase of regioselectivity in the Negishi reaction of dihalophenanthrolines can be achieved by the preparation of halo-substituted derivatives bearing different halogen atoms at the phenanthroline core. Interesting example is 3,8-dibromo-4,7-dichloro-1,10-phenanthroline in which γ-Cl substituents are activated to the substitution but bromides are known to be more reactive in the oxidative addition step of the catalytic cycle compared to chlorides in cross-coupling reactions. The reaction of

3,8-dibromo-4,7-dichloro-1,10-phenanthroline with mesitylene Zn derivative selectively led to the 3,8-disubstituted product which is a valuable intermediate compound in the synthesis of highly substituted Phen ligands (Scheme 15).



Scheme 15. The Negishi reaction of 3,8-dibromo-4,7-dichloro-1,10-phenanthroline.

It is also worth noting, that the Negishi and Sonogashira reactions can be regarded as complimentary synthetic tools for $C(sp^2)$–C(sp) bond formation. The Negishi coupling sometimes gives better results compared to coupling under Sonogashira conditions as it was demonstrated reacting 3,5,6,8-tetrabromophenanthroline with phenylacetylene (Scheme 16).[90] Employing Cl–Zn-phenylacetylenide as reagent, the yield of the target product was increased from 15% obtained in the Sonogashira reaction to 60%. However, a specific catalyst (see a footnote of Table 1) was required for the successful Negishi coupling (Scheme 16).



Y = H i) 12 mol% $Pd(PPh_3)_4$, DMF-NEt_3 (2/1), 150°C, 47 h; yield 15%
Y = ZnCl ii) 20 mol% CAT, NMP-THF (1.15/1), 150°C, 7 h; yield 60%

Scheme 16. Synthesis of 3,5,6,8-tetra(phenylethynyl)-1,10-phenanthroline *via* the Sonogashira and Negishi reactions.

3.1.5. Kumada cross-coupling

Quite rare is the use of the Kumada coupling in the Phen synthetic chemistry. It seems that the better tolerance of the Suzuki-Miyaura, Negishi and Stille reactions for various functional groups decreases the interest in this method for C–C bond formation.

It was reported that the Kumada reaction can be used for functionalization of low reactive 3- and 3,8-disubstituted 1,10-phenanthrolines. The reaction is conducted under classical conditions using $NiCl_2$(DPPP) (DPPP=1,3-bis(diphenylphosphino)propane) complex as a catalyst and sometimes the product yield can be increased by optimizing the reaction temperature. For example, Huang and co-workers proposed to initiate the reaction at room temperature and afterwards they applied prolonged heating.[99-101] 3-(Thiophen-2-yl)- and 3,8-bis(thiophen-2-yl)-substituted Phens were obtained in 73-91% yields under these conditions. Running the reaction at room temperature resulted in lower yield (40%) of the target product (Scheme 17).[102]

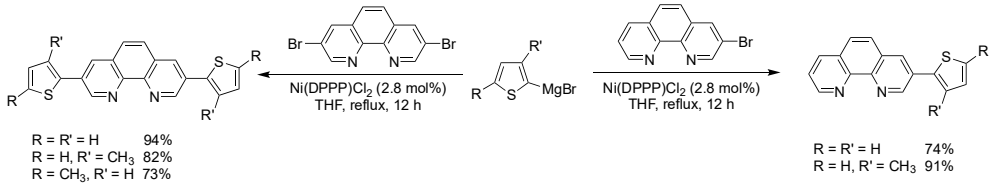
3.1.6. Mizoroki-Heck cross-coupling

To our knowledge, only two examples of the Mizoroki-Heck reaction for Phen derivatives were reported, both by Ajibade and Adeloye.[103,104] The reactions were run with *trans*-2,3-dimethylacrylic acid using Pd(0) as a catalyst, and the target compounds were obtained in good yields (Scheme 18).

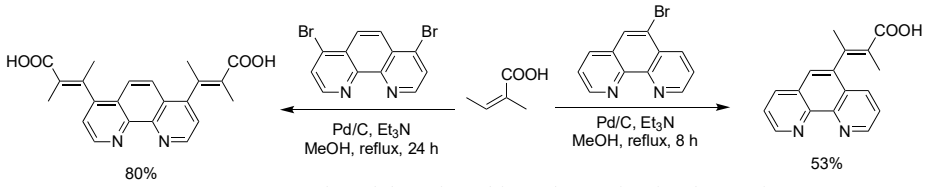
Alternatively, vinyl-substituted Phens can be prepared in two steps from methylated Phens using consecutive formylation and the Wittig coupling reactions.[105] The Stille reaction is also helpful to prepare these derivatives with extended aromatic system.

3.1.7. Reductive dimerization

The synthesis of bis-1,10-phenanthrolines was reported long ago[106] and was revisited after the development of catalytic approaches to the dimerization of aryl halides.



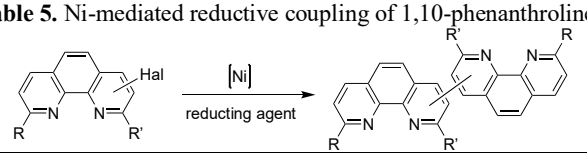
Scheme 17. Functionalization of Phens *via* the Kumada reaction.



Scheme 18. Examples of the Mizoroki-Heck reaction in Phen series.

The reported reactions of the reductive dimerization of halo-Phens mediated by Ni(0) complexes are summarized in Table 5. 2-Chloro-1,10-phenanthroline was the first halide of Phen series which was involved in this reaction by Rice and Anderson[107] using conditions developed for aryl chlorides by Iyoda and coworkers.[108] The reaction was conducted using $NiCl_2(PPh_3)_2$ pre-catalysts in the presence of zinc dust (for reduction of nickel(II) ions) and tetraethylammonium iodide in refluxed THF. The dimer was isolated in only 30% yield which was increased more than twice after employing the nickel salt in stoichiometric amount and performing the reaction in DMF (entries 10 and 11). Using these experimental conditions all isomeric bis-1,10-phenanthrolines as well as their alkyl- and aryl-substituted derivatives were prepared in good yields. Interestingly, the positive role of ammonium iodide was demonstrated for the dimerization of various aryl chlorides[108] but was not investigated in detail for Phen derivatives.

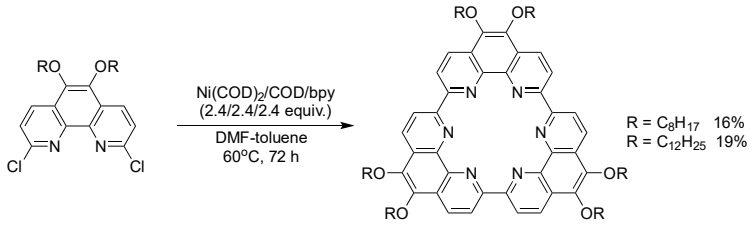
Table 5. Ni-mediated reductive coupling of 1,10-phenanthrolines.



Entry	Position	Hal	R	R'	Reagents	[Ni]	Reaction conditions	Yield, (%)	Ref.
1	5	Cl	H	H	Zn, $[Et_4N]I$	$NiCl_2{\cdot}6H_2O/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C, 14 h	71	[109]
2	5	Br	H	H	-	$Ni(COD)_2$/COD/bpy[a] (1.1/1.1/1.1 equiv.)	DMF, 85 °C, 24 h	35	[110]
3	5	Br	Bu	Bu	-	«	DMF, 55 °C, 24 h	10	[110]
5	4	Cl	H	H	Zn, $[Et_4N]I$	$NiCl_2{\cdot}6H_2O/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C 14 h	66	[109]
6	3	Br	H	H	Zn	$NiCl_2/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C, overnight	70	[111]
7	3	Br	H	H	Zn, $[Et_4N]I$	$NiCl_2{\cdot}6H_2O/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C, 14 h	62	[109]
8	3	Br	Ar[b]	H	Zn	$NiCl_2{\cdot}6H_2O/PPh_3$	DMF, 50 °C	n.d.[c]	[112]
9	2	Cl	H	H	Zn, $[Et_4N]I$	$NiCl_2(PPh_3)_2$ (10 mol%)	THF, reflux, 12 h	30	[107]
10	2	Cl	H	H	Zn	$NiCl_2/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C, overnight	80	[111]
11	2	Cl	H	H	Zn, $[Et_4N]I$	$NiCl_2{\cdot}6H_2O/PPh_3$ (1.2/4 equiv.)	DMF, 55 °C,14 h	71	[109]

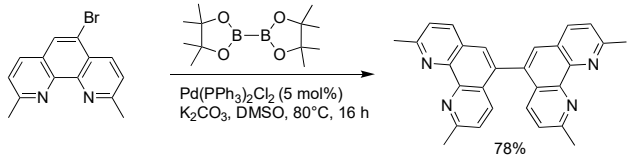
[a]COD=cycloocta-1,5-diene. [b]Ar=*p*-$MeOC_6H_4$, *p*-tolyl, mesityl. [c]n.d.=not determined.

Comparing the results obtained by different groups (entries 6 and 7, 10 and 11, respectively), it seems that this additive can be omitted at least in the preliminary experiences focusing on the preparation of unknown dimers *via* this strategy. Attempts to replace $NiCl_2$/triphenylphosphine by $Ni(COD)_2$/COD/bpy system which works well for 2,2'-bipyridyl derivatives[113] were inconclusive because the target products were obtained in low yields (entries 2 and 3).[110] Nevertheless, these conditions were successfully applied for the synthesis of the macrocyclic ligands bearing three 1,10-phenanthroline residues in the cycle (Scheme 19).[82]



Scheme 19. Synthesis of the macrocyclic ligand *via* the reductive trimerization of 2,9-dichloro-1,10-phenanthroline derivatives.

It is also worth noting that Phen dimers can be obtained from halo-substituted Phens through the tandem Miyaura/Suzuki-Miyaura coupling. This synthetic approach is still limited to rare examples such as the dimerization of 5-bromoneocuproine (Scheme 20).[114] 5-Bis-1,10-neocuproine was obtained in 78% yield by reacting this dihalide with bis(pinacolato)diboron in the presence of $PdCl_2(PPh_3)_2$ and potassium carbonate in DMSO at 80 °C.



Scheme 20. Synthesis of 5-bis-1,10-neocuproine according to the tandem Miyaura/Suzuki-Miyaura coupling.

3.2. C–Het coupling

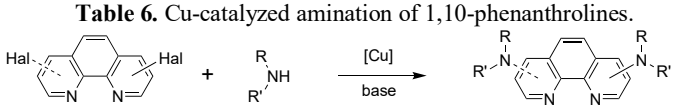
The C–Het coupling reactions with Phens are limited to the introduction of nitrogen-, phosphorous- and boron-containing substituents at the heterocycle.

3.2.1. Pd- and Cu-catalyzed amination reactions

Among Phens bearing heteroatoms directly attached to the heterocyclic core, amino-substituted derivatives are widely investigated in sensing and supramolecular chemistry. The amination of α and γ positions of pyridine rings can be performed according the nucleophilic substitution of activated chlorine atoms in α- or γ-chloro-substituted Phens. However, the scope of this reaction is limited to reactive sterically unhindered aliphatic amines. Catalytic amination reactions allow to introduce less nucleophilic aromatic amines in these positions and they are also useful for the preparation of β and δ isomers which were inaccessible *via* the catalyst-free reactions. Both Cu- and Pd-catalyzed amination reactions were reported with Phens but both of them required a careful optimization to obtain target products in preparative yields.

Cu-catalyzed coupling is only used for substitution of bromine and iodine by azole (imidazole, pyrazole and carbazole) residues using cuprous iodide or cupric sulfate under harsh conditions (Table 6). Soluble copper complexes which allow to perform the amination and amidation reactions under mild conditions[115,116,117] are inefficient for functionalization of Phens probably due to a high affinity of Phen chelators to both Cu(I) and Cu(II) ions.

Table 6. Cu-catalyzed amination of 1,10-phenanthrolines.

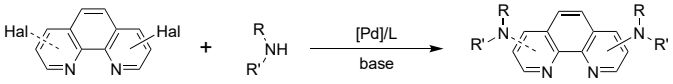


Entry	Posi-tion(s)	Hal	Amine	Catalyst (mol%)	Reaction conditions	Yield, (%)	Ref.
1	3	Br	carbazole	CuI (20)	K_2CO_3, nitrobenzene 200 °C, 24 h	40	[118]
2	3,8	Br	imidazole	$CuSO_4$ (2.5)	K_2CO_3, neat, 180 °C, 4 h	70	[119]
3	2	I	pyrazole	CuI (10)	K_2CO_3, DMSO, 100 °C, 96 h	70	[120]
4	2	I	pyrazole	«	K_2CO_3, DMSO, 160 °C, 96 h	85	[121]
5	2	I	2-methylimidazole	«	K_2CO_3, DMSO, 160 °C, 96 h	77	[121]
6[a]	2	I	1,2,4-triazole	«	K_2CO_3, DMSO, 160 °C, 96 h	62	[121]

[a]Heteroarylation proceeds at the position 1 of triazole.

Buchwald-Hartwig amination reaction[122,123] which proceeds in the presence of palladium(0) complexes with phosphines is a much more efficient strategy for the functionalization of Phens (Table 7). It was recognized that this catalytic cross-coupling is difficult to perform in the case of *N*-chelators and heterocycles which readily coordinate transition metal ions removing them from the catalytic cycle.[124,125] Nevertheless, the reactions of Phen halides with reactive diarylamines and cyclic secondary amines can be performed using classical $Pd_2(dba)_3$/BINAP catalytic system (entries 1, 2, 5 and 12). Other reactions demand an optimization because the extensive reduction of the halide is commonly observed in the reaction mixtures.

Table 7. Buchwald-Hartwig amination of 1,10-phenanthrolines.



Entry	Position(s)	Hal	Amine	Catalyst (mol%)	Reaction conditions	Yield, (%)	Ref.
1[a]	5	Br	*n*-Bu-NH_2	$Pd_2(dba)_3$/BINAP[b] (5/10)	*t*BuONa, toluene, reflux, 1 h	54	[129]
2	5	Br	*N*-Boc-piperazine	«	*t*BuONa, toluene, reflux, 16 h	80	[130]
3	5	Br	2-(1-adamantyloxy) ethanamine	$Pd(dba)_2$/Josiphos[c] (8/9)	*t*BuONa, dioxane, reflux, 24 h	63	[126]
4	4	Cl	2-(1-adamantyloxy) ethanamine	-	K_2CO_3, DMF, reflux, 24 h	37	[126]
5	4	Cl	2-(1-adamantyloxy) ethanamine	$Pd(dba)_2$/BINAP (4/4.5)	Cs_2CO_3, dioxane, reflux, 24 h	49	[126]
6	4,7	Br	2-(1-adamantyloxy) ethanamine	«	Cs_2CO_3, dioxane, reflux, 24 h	58	[126]
7[d]	4,7	Br	2-(1-adamantyloxy) ethanamine	«	Cs_2CO_3, dioxane, reflux, 24 h	74	[126]
8	4,7	Cl	(4-*tert*-Bu-Ph)$_2$NH	$Pd(OAc)_2$/*t*Bu_3P (4/8)	*t*BuONa, *o*-xylene, reflux, 8 h	47	[131]
9	3	Br	2-(1-adamantyloxy) ethanamine	$Pd(dba)_2$/Josiphos (8/9)	*t*BuONa, dioxane, reflux, 24 h	60	[126]
10	3,8	Br	Ph_2NH	$Pd_2(dba)_3$/Xantphos[e] (12/31)	*t*BuONa, toluene, 100 °C, 24 h	56	[132]
11	3,8	Br	carbazole	«	*t*BuONa, toluene, 100 °C, 24 h	30	[132]
12	3,8	Br	phenoxazine	«	*t*BuONa, toluene, 100 °C, 24 h	83	[132]
13	2	Br	1,5,7-triazabicyclo-[4.4.0]dec-5-ene	$Pd(OAc)_2$/BINAP (2/3)	*t*BuOK, toluene, 90 °C, 3 h	87	[133]
14	2,9	Cl	2-aminopyridine	$Pd_2(dba)_3$/DPPF	AcONa, toluene, 100 °C, 60 h	75	[128]

[a]5-Bromo-2,9-dimethy-1,10-phenanthroline was used. [b]BINAP=2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.
[c]Josiphos=(R)-1-[(S_P)-2-(diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine.
[d]4,7-Dibromo-2,9-dimethyl-1,10-phenanthroline was used. [e]Xantphos=4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

Another competing reaction which highly influences the product yields in the amination of γ-halo-Phens performed in the presence of sodium *tert*-butylate is the nucleophilic substitution affording 4-*t*BuO-substituted Phens.

As shown in Table 7, many phosphine ligands such as tBu$_3$P, DPPF, Xantphos (entries 8, 10 and 14) which are efficient for the amination of aryl halides can be employed for Phen functionalization. Unfortunately, experimental conditions should be adjusted using the basic trial-and-error method. The Josiphos ligand can be recommended for the reactions with most reluctant substrates such as sterically hindered primary amines (entries 4 and 6) or less reactive β- and δ-halophenanthrolines (entries 3 and 9).[126] In addition, cesium carbonate seems to be the most appropriate base to perform the reaction of α- and γ-chloro-1,10-phenanthrolines with primary amines (entries 5-7).

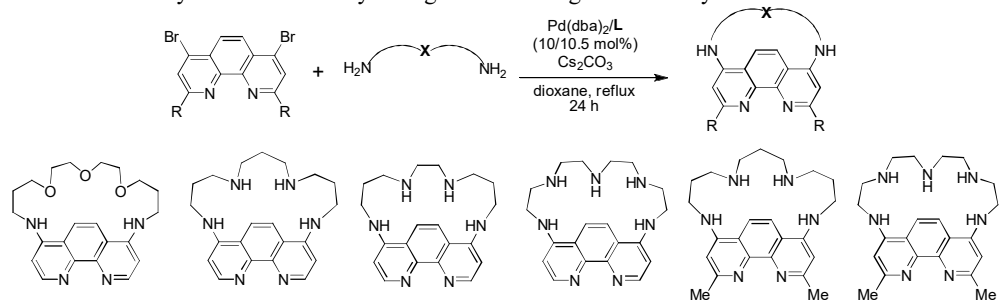
It is of interest to compare the reaction of 4-chloro-1,10-phenanthroline with 2-(1-adamantyloxy)ethanamine conducted under the catalyst-free conditions (entry 4) and in the presence of Pd(dba)$_2$/BINAP (entry 5). The yield of the product is slightly increased (from 37% to 49%) in the Pd-catalyzed reaction indicating that catalytic conditions may be useful even for the amination of most reactive Phen halides.

Finally, the steric hindrances at the 1,10-phenanthroline *N,N*-chelating site introduced by two methyl substituents at α position of the pyridine ring have a positive effect on the product yield (entry 7). The amination of 4,7-dibromo-2,9-dimethylphenanthroline with 2-(1-adamantyloxy)ethanamine (Pd(dba)$_2$/BINAP, Cs_2CO_3, entry 7) gave the target product in 74% yield which is higher compared to that observed in the amination of 4,7-dibromophenanthroline (entry 6).[126]

In contrast to the substitution of two halogen atoms of aryl dihalides,[127] the sequential reactions of two halogen atoms located at different pyridine rings of Phen core by amine residues afford the product in the yields comparable to those observed in the amination of mono-halides because electronic effects of the amino substituent do not perturb the second amination reaction (entries 6-8, 10-12 and 14).[128]

In spite of the need in the adjustment of the reaction conditions to the structure of Phen halide and amine, Pd-catalyzed amination reaction is a useful synthetic tool to prepare unusual ligands for many practical applications. For instance, it was employed for the one-pot synthesis of a novel series of *N*- and *O*-containing macrocyclic ligands which display an externally directed 4,7-amino-1,10-phenanthroline moiety (Table 8).

Table 8. Synthesis of macrocyclic ligands according the Pd-catalyzed amination reaction.



A **B** **C** **D** **E** **F**

Entry	R	Product	Ligand, L	Cs_2CO_3, (equiv.)	Yield, (%)
1	H	**A**	BINAP	4	20
2	H	**B**	BINAP	10	5
3	H	**B**	Josiphos	10	35
4	H	**B**	Josiphos	4	10
5	H	**C**	Josiphos	10	17
6	H	**D**	Josiphos	10	25
7	Me	**E**	BINAP	10	33
8	Me	**F**	BINAP	10	30

The macrocyclization of 4,7-dibromo-1,10-phenanthrolines with linear polyoxadiamines proceeds in the presence [Pd(dba)$_2$]/BINAP catalytic system employed with Cs_2CO_3 in dioxane at reflux (entry 1). Linear polyamines are well-known chelators for the palladium(II) ion, which complicates their use in Pd-catalyzed amination reactions.[127] Therefore, it is not surprising that the [Pd(dba)$_2$]/BINAP catalytic system employed with Cs_2CO_3 in dioxane at reflux demonstrated very poor efficiency in this macrocyclization reaction (entry 2). On the contrary, [Pd(dba)$_2$]/Josiphos afforded macrocycles in reasonable yields when the amount of cesium carbonate was increased up to 10 equivalents (entries 3 and 4). Interestingly, that more reactive 2,9-dimethyl-substituted dibromide reacts with linear polyamines in the presence of the less expensive [Pd(dba)$_2$]/BINAP catalyst affording the product in similar yields (entries 7 and 8).

It is worth noting that the catalyst-free nucleophilic substitution is not suitable for the preparation of these macrocyclic ligands even with polyamines bearing protected secondary amino groups because it demands dilution and stoichiometric amounts of the reagents. Sensing properties of ditopic ligands thus prepared were briefly investigated after their coordination to Ru(II) reacting the ligands with Ru(bpy)$_2$Cl$_2$.[126] One of these complexes exhibits a selective dual-channel (UV-vis and fluorescence) response on the presence of Cu(II) ions in the studied solutions.

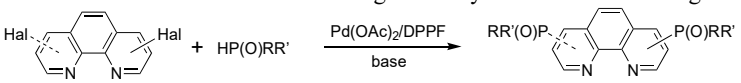
3.2.2. C–P bond forming reactions

Phosphorous containing Phens have been attracted considerable interest for a long time as promising ligands for catalysis, ligands for separation of actinides from lanthanides and valuable building blocks in supramolecular chemistry.[134-137]

Hirao reaction[138,139] was the first Pd-catalyzed C–P bond forming reaction which was successfully employed by us to introduce the diethoxyphosphoryl substituent at all carbon atoms of the heterocyclic core (Table 9).[140] The products were obtained in good yields reacting bromides with diethyl phosphite using palladium(II) acetate and bidentate phosphine ligand (DPPF) while classical triphenylphosphine was inefficient in this transformation (entries 1, 2 and 3). Interestingly, readily available α- and γ-chlorophenanthrolines also smoothly reacted under these conditions (entries 3 and 8). Diphosphonates were prepared in good yields through the phosphonylation of dihalides (entries 4, 5, 7 and 10). The new synthesized phosphonate derivatives are of interest for obtaining unusual polynuclear complexes, water soluble catalytic systems and for development of stable heterogenized catalytic systems.[141-144]

Recently, Borisova and coworkers have shown that Pd(OAc)$_2$/DPPF catalytic system works well for coupling of 2-chloro- and 2,9-dichloro-1,10-phenanthrolines with secondary phosphine oxides in DMF (entries 11, 12 and 13).[145] This is a promising one-step synthetic approach to hard- and soft phosphine oxide receptors for *f*-element complexation that can replace classical non-catalytic synthetic methods.[136,146]

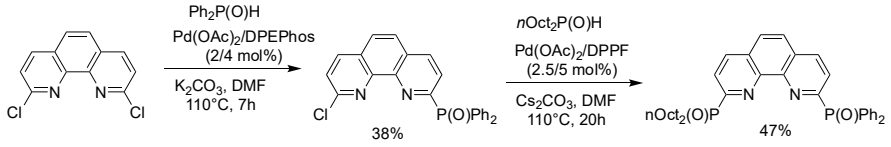
Table 9. Functionalization of Phens according Pd-catalyzed C–P bond forming reactions.



Entry	Position(s)	Hal	R	R'	Catalyst, (mol%)	Conditions	Yield, (%)	Ref.
1	5	Br	OEt	OEt	5/10	Et_3N, toluene, reflux, 20 h	80	136
2	4	Br	OEt	OEt	10/20	Et_3N, dioxane, reflux, 12 h	52	136
3	4	Cl	OEt	OEt	10/20	Et_3N, dioxane, reflux, 12 h	55[a]	143
4	4,7	Br	OEt	OEt	10/20	Et_3N, toluene, reflux, 20 h	71	136
5	4,7	Cl	OEt	OEt	10/20	Et_3N, toluene, reflux, 20 h	69[a]	143
6	3	Br	OEt	OEt	5/10	Et_3N, toluene, reflux, 5 h	81	140
7	3,8	Br	OEt	OEt	10/20	Et_3N, toluene, reflux, 5 h	70	140
8	2	Cl	OEt	OEt	10/20	Et_3N, toluene, reflux, 20 h	71	140
9	2	Cl	Ph	Ph	1/2	K_2CO_3, DMF, 120 °C, 7 h	98	146
10	2,9	Cl	OEt	OEt	10/20	Et_3N, toluene, reflux, 3 h	80	140
11	2,9	Cl	Ph	Ph	2/4	K_2CO_3, DMF, 80 °C, 7 h	79	145
12	2,9	Cl	Ph	*t*Bu	2/4	K_2CO_3, DMF, 80 °C, 7 h	71	145

[a]Unpublished data.

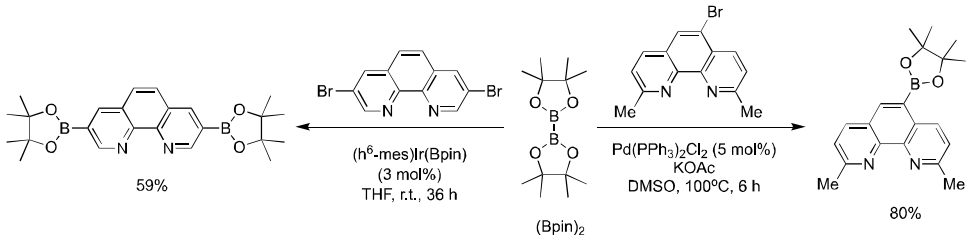
Unsymmetrical diphosphoryl-substituted Phens were only obtained according to a stepwise reaction of 2,9-dichloro-1,10-phenanthroline with substoichiometric amounts of phosphine oxides (Scheme 21).[148] However, the regioselectivity of the first coupling was quite low even when DPPF was replaced by DPEPhos (DPEPhos=(oxydi-2,1-phenylene)bis(diphenylphosphine)) ligand.



Scheme 21. Synthesis of unsymmetrical diphosphoryl-substituted Phen *via* the Pd-catalyzed coupling reaction.

3.2.3. Miyaura-Ishiyama coupling

Borylation of halo-substituted Phens has been accomplished in high yields using Pd[57] and Ir[96] catalysts (Scheme 22) but boron-containing Phens are still rarely used as intermediate compounds in the preparation of functionalized ligands. These compounds can form intermolecular complexes by boron coordination to the nitrogen atoms of the heterocycle what probably causes inconveniences for their purification and handling.



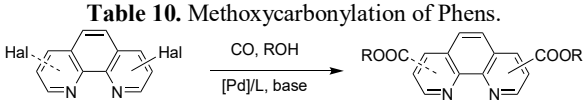
Scheme 22. Catalytic borylation of bromo-1,10-phenanthrolines.

3.3. Alkoxycarbonylation

The alkoxycarbonylation of aryl halides mediated by low-valent palladium(0) was pioneered by Heck[149] and applied to functionalization of reactive 2,9-dichloro-1,10-phenanthroline by Zeissel and El-ghayoury.[150]

Later the experimental conditions for the ester preparation from all isomeric halogen-substituted Phens were reported (Table 10).

Table 10. Methoxycarbonylation of Phens.



Entry	Position(s)	Hal	R	Reagent	Catalyst [Pd]/L (mol%)	Conditions	Yield, (%)	Ref.
1	5	Br	Me	CO, Et_3N	$PdCl_2(PPh_3)_2$ (5)	MeOH, 100 °C, 4 bar, 6 h	66	154
2[a]	4	Br	Me	CO, Et_3N	$Pd(dba)_2$/DPPP (5/5)	MeOH, 150 °C, 30 bar, 16 h	44	14
3	3	Br	*n*Bu	CO, K_2CO_3	$Pd(OAc)_2$/Xantphos (4/8)	*n*BuOH, 90 °C, 1 bar, 3 h	66	151
4	3,8	Br	*n*Bu	CO, K_2CO_3	$Pd(OAc)_2$/Xantphos (5/10)	*n*BuOH, 90 °C, 1 bar, 3 h	70	151
5[b]	3,8	Br	H	*N*-formyl-saccharin, KF	$Pd(OAc)_2$/Xantphos (6/9)	DMF, 80 °C, 72 h	81	152
6	2,9	Cl	*n*Bu	CO, Bu_3N	$PdCl_2(PPh_3)_2$ (2)	*n*BuOH, 120 °C, 1 bar, 72 h	60	150
7	2	Cl	*n*Bu	CO, Bu_3N	$PdCl_2(PPh_3)_2$ (2)	*n*BuOH, 120 °C, 1 bar, 72 h	62	150
	9	Br						

[a]4-Bromo-7-methyl-1,10-phenanthroline was used. [b]The target 3,8-dicarboxy-1,10 phenanthroline was obtained after hydrolysis of intermediate compound in Et_3N-water mixture (7:10 v/v) at room temperature.

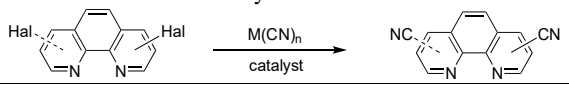
The reactions were commonly conducted in refluxing alcohols in a continuous flow of carbon monoxide at atmospheric pressure with palladium(0) complexes with triphenylphosphine or bidentate phosphine ligands such as Xantphos (entries 2-4, 6 and 7). The best choice of alcohol is determined by a solubility of the starting halide and the target ester. Methoxycarbonylation, which is commonly used for the synthesis of aryl carboxylic acids, was rarely performed in Phen series, probably due to a low solubility of methyl phenanthrolinylcarboxylates. For instance, the methoxycarbonylation of 3,8-dibromo-1,10-phenanthroline in methanol in the presence of $Pd(OAc)_2$/Xantphos afforded a mixture of 3-(methoxycarbonyl)- and 3,8-di(methoxycarbonyl)-1,10-phenanthrolines, which were found to be inseparable by column chromatography.[151] In contrast, pure 3,8-di(butoxycarbonyl)-1,10-phenanthroline can be isolated in good yield performing the ester synthesis in *n*-butanol.

Methoxycarbonylation of 4-bromo and 5-bromo-1,10-phenanthrolines was carried out in autoclave at 100-150 °C (entries 1 and 2), but comparative studies at atmospheric pressure were not reported in both cases. Farha, Delferro and coworkers[152] employed *N*-formylsaccharin as a source of carbon monoxide (entry 5) following the earlier reported procedure for the preparation of acids from aryl halide.[153]

3.4 Cyanation

Palladium-catalyzed cyanation reaction[155] successfully proceeds with Phen derivatives though the number of examples is limited (Table 11). Dibromo-substituted Phens were reacted with sodium cyanide using the $Pd(OAc)_2$/DPPENT catalytic system and TMEDA as a base in mesitylene under reflux (entries 1, 2 and 5).[156] To performed the reaction with chloro-substituted Phens, the conditions developed for aryl chlorides[158] proved to be suitable (entries 3 and 4). 4-Chloro- and 4,7-dichloro-1,10-phenanthrolines were transformed into corresponding cyanides using $Zn(CN)_2$ as a cyanide source, the $Pd(dba)_2$/DPPF catalytic system and a catalytic amount of zinc powder. The use of microwave assistance in these reactions allowed to shorten the reaction time and to lower catalyst loading without diminishing the yields.[157] The cyanides thus prepared are convenient intermediate compounds in the synthesis of amides or oximes according to standard methods.

Table 11. Cyanation of Phens.



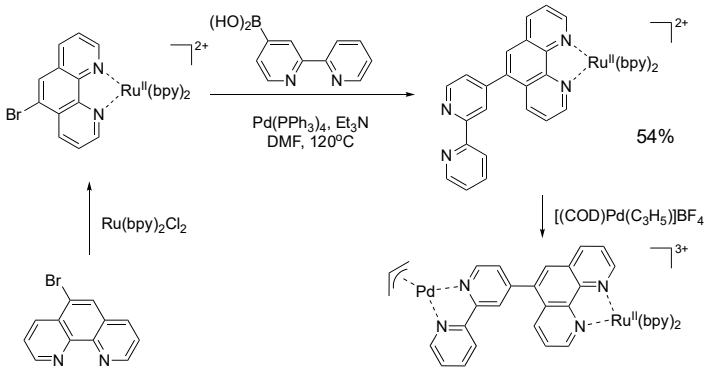
Entry	Position(s)	Hal	$M(CN)_n$	Catalyst (mol%)	Conditions	Yield, (%)	Ref.
1	5,6	Br	NaCN	$Pd(OAc)_2$/DPPENT[a] (5/20)	TMEDA, mesitylene, reflux, 12 h	52	156
2	4,7	Br	NaCN	«	TMEDA, mesitylene, reflux, 12 h	60	156
3	4	Cl	$Zn(CN)_2$	$Pd(dba)_2$/DPPF/Zn (2/2/10)	DMA, 130 °C (MW), 1 h	70	157
4	4,7	Cl	$Zn(CN)_2$	$Pd(dba)_2$/DPPF/Zn (6/6/10)	DMA, 130 °C (MW), 1 h	65	157
5	3,8	Br	NaCN	$Pd(OAc)_2$/DPPENT (5 /20)	mesitylene, reflux, 12 h	62	156

[a]DPPENT=5-bis(diphenylphosphino)pentane.

4. Functionalization of metal complexes with 1,10-phenanthroline ligands

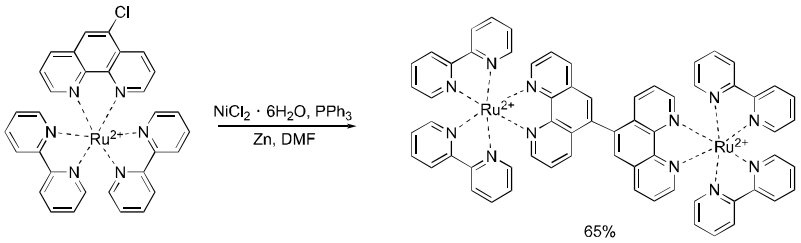
Functionalization of metal complexes with 1,10-phenanthroline ligands is a synthetic alternative to the preparation of the complexes by the metal coordination to already modified chelators. This synthetic strategy is useful for the preparation of thermodynamic stable and inert complexes such as Ru(II), Ir(III), Os(II) complexes with Phen ligands. These syntheses of TM complexes allow to avoid binding the catalyst with phenanthroline substrates and to increase the reactivity of Phens due to electron-accepting capacity of positively charged metal ions. These benefits are balanced by the demands of specific techniques for the purification of polar complexes which are hardly compatible with classical column chromatography. Nevertheless, in some cases this strategy is the only possible, especially in the synthesis of polynuclear complexes when the selective coordination of polytopic ligands cannot be easily achieved.

For instance, Pd(II)–Ru(II) bimetallic complexes were prepared according to this approach (Scheme 23).[159] First, the Suzuki-Miyaura reaction was employed for the functionalization of the Ru(II) complex by the bpy residue. Then the chelator thus obtained was coordinated to Pd(II) ions in order to obtain the bimetallic catalyst.



Scheme 23. Suzuki-Miyaura reaction in the synthesis of dinuclear Pd(II)–Ru(II) complex.

The reductive dimerization of the Ru(II) complex with 5-chloro-1,10-phenanthroline was successfully carried out in the presence of Ni(0) catalyst, and the target product was isolated in a good yield (Scheme 24).[160]



Scheme 24. Reductive dimerization of the ruthenium(II) complex with 5-chloro-1,10-phenanthroline.

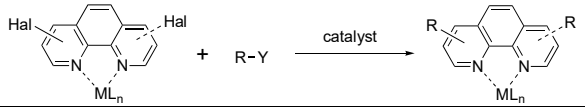
This method was also used for the synthesis of Ir(III) and Os(II) complexes which were obtained in comparable yields. In contrast, attempt to perform the dimerization of metal-free 5-chloro-1,10-phenanthroline by using the same reaction conditions failed.

Some of other examples of coupling reactions in metal complexes with halo-substituted Phens are summarized in Table 12. The most abundant are reactions of Ru(II) and Ir(III) complexes, in particular the Suzuki-Miyaura and Sonogashira couplings affecting β, γ and δ positions of the heterocycle. For instance, Sonogashira coupling using the Ru(II) complex with 5-chloro-1,10-phenanthroline gave the product in 65% yield (entry 9),[47] while the analogous reaction of 5-chloro-1,10-phenanthroline provided substantially lower product yield.[45] Rhenium(I) carbonylates are more difficult substrates which generally afford poorer yields in similar reactions due to the ligand exchange between the complex and the catalyst (entry 13).

The Sonogashira reaction involving the Pt(II) complex with 5-bromo-1,10-phenanthroline was also accompanied by the side ligand exchange reaction; in this case the chloride ligand in the coordination sphere of platinum atom was replaced by the acetylenide ligand (entry 8). Recently, these reactions have found interesting application in the synthesis of cross-linked polymers: *e.g.* the Stille coupling employing distannyl substituted aromatic compounds and Ru(II) complexes with 3,8-dibromo-1,10-phenanthroline afforded fluorescent polymers (entry 21).[170] Analogous approach using the Mizoroki-Heck reaction provided Co(II)- and Zn(II)-containing phenanthroline-based polymers (entry 19).[169]

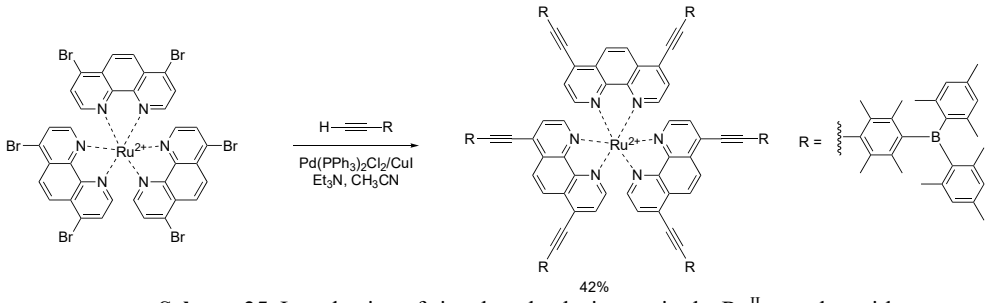
The Pd-catalyzed coupling reactions can be carried out in several ligands coordinated to a metal center. Thus, the Sonogashira reaction allows to prepare the hexasubstituted Ru(II) complex containing three di(ethynyl)phenanthroline ligands by the substitution of six bromine atoms in the starting complex (Scheme 25).[172]

Table 12. Catalytic functionalization of 1,10-phenanthroline complexes.



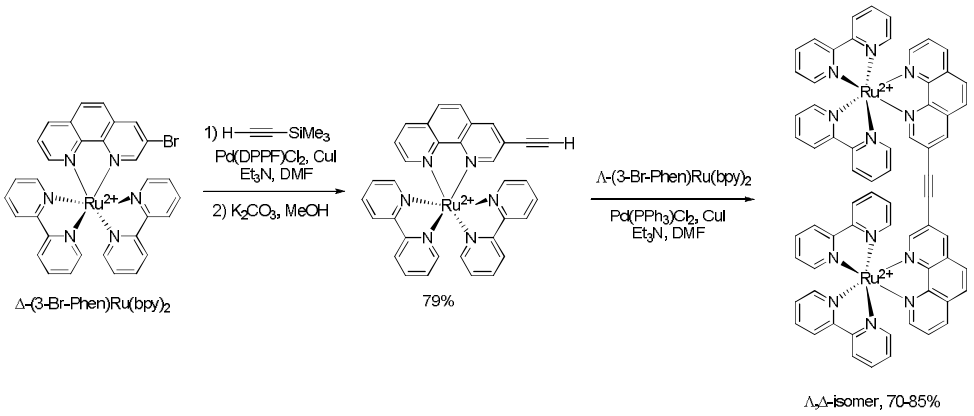
Entry	Position(s)	Hal	ML_n	Reaction	Catalyst	Yield, (%)	Ref.
1	5	Br	Ru(4,4'-bis(*t*Bu)bpy)$_2$	Suzuki-Myaura	$PdCl_2(PPh_3)_2$	97	161
2	5	Br	Ru(4,4'-bis(*t*Bu)bpy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	73	162
3	5,6	Br	Ru(4,4'-bis(*t*Bu)bpy)$_2$	Suzuki-Myaura	$PdCl_2(PPh_3)_2$	68	161
4	5,6	Br	Ru(4,7-bis(Ph)Phen)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	57	46
5	5	Br	Ir(ppy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	54	163
6	5,6	Br	Ir(ppy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	62	163
7	5	Br	Ir(ppy)$_2$	Suzuki-Myaura	$Pd(OAc)_2$	76	164
8	5	Br	$PtCl_2$[a]	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	25[a]	36
9	5	Cl	Ru(bpy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	65	47
10	4	Cl	Ru(bpy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	85	47
11	4,7	Cl	Ru(bpy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	75	47
12	4	Br	Ru(Phen)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	50	165
13	4	Br	$Re(CO)_3Br$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	15	166
14	4,7	Br	$Re(CO)_3Br$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	69	167
15	3	Br	Ru(bpy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	75	47
16	3	Br	Ir(ppy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	59	163
17	3,8	Br	Ir(ppy)$_2$	Suzuki-Myaura	$Pd(PPh_3)_4$	75	168
18	3,8	Br	Ir(ppy)$_2$	Sonogashira	$PdCl_2(PPh_3)_2$/CuI	63	163
19	3,8	Br	Co(3,3'-bis(COOH)bpy)$_2$(OAc)$_2$	Mizoroki-Heck	$Pd(OAc)_2$/P(*o*-Tol)$_3$	41	169
20	3,8	Br	Zn(3,3'-bis(COOH)bpy)$_2$(OAc)$_2$	Mizoroki-Heck	$Pd(OAc)_2$/P(*o*-Tol)$_3$	45	169
21	3,8	Br	Ru(4,4'-bis($C_{10}H_{21}$)bpy)Cl_2	Stille coupling	$Pd(PPh_3)_4$	32	170
22	2,9	Br	$Re(CO)_3Br$	Suzuki-Myaura	$Pd(OAc)_2/PPh_3$	30	171

[a]Substitution of chlorine atom for alkyne residue in the coordination sphere of Pt was observed.



Scheme 25. Introduction of six ethynyl substituents in the Ru^{II} complex with 4,7-dibromo-1,10-phenanthroline according the Sonogashira reaction.

Catalytic reactions were also used in the synthesis of nonracemic complexes. For instance, it was found possible to resolve Δ and Λ isomers of Ru(II) complex bearing 3-bromo-1,10-phenanthroline and 2,2'-bipyridine ligands. Kinetical inertness of these complexes allows for their chemical transformations with the retention of configuration. Using the Sonogashira coupling, Tzalis and Tor managed to synthesize all possible stereoisomers (ΔΛ, ΔΔ and ΛΛ) of binuclear complexes and studied their photophysical properties (Scheme 26).[173]



Scheme 26. Synthesis of chiral dinuclear ruthenium(II) complexes *via* the Sonogashira coupling.

5. Conclusion

Phen is a classical ligand in coordination chemistry which is renowned among bidentate nitrogen ligands for the exceptional properties of its stable metal complexes. Rapid development of synthetic approaches to Phen derivatives has been promoted by the increase of the interest in their complexes in many fundamental and practical applications. During last three decades TM-catalyzed cross-coupling reactions have become a powerful tool for the synthesis of Phen ligands. They allow for the preparation of 3- and 5-substituted derivatives which are hardly available through other synthetic approaches. Moreover, they are expanded beyond the scope of the nucleophilic substitution reaction for other isomeric halo-substituted phenanthrolines. Among different TM catalysts, palladium complexes seem to be the most efficient for the functionalization of these bidentate chelators. The Suzuki-Miyaura and Sonogashira reactions allow for the C–C bond formation at all positions of the heteroaromatic scaffold in the presence of available and simple catalytic systems. However, in many other cases the catalytic processes are hindered by the coordination properties of these bidentate ligands, thus demanding a fine adjustment of the catalytic systems. In some cases, the application of 1,10-phenanthroline metal complexes as substrates in TM-catalyzed reactions is also possible provided the complexes possess enough high kinetic and thermodynamic stability to prevent their degradation in the course of catalytic transformations. Comparing catalytic chemistry of Phens with that of other aromatic derivatives, it is worth noting that many synthetic methods, such as C–Het (Het=O, S) coupling, direct C–H functionalization, and selective $C(sp^3)$–$C(sp^2)$ bond formation, are still underdeveloped for these compounds. Thus, we expect that the merge of the catalytic chemistry with Phen chelators will bring forward not only novel amazing reactions in which Phens serve as ligands but also useful synthetic approaches for the preparation of these ligands.

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