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Mild copper-catalyzed *N*-arylation of azaheterocycles with aryl halides

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Abstract—A highly efficient copper(I)-catalyzed *N*-arylation of azaheterocycles with various aryl halides is reported. The *N*-arylation reaction can be carried out using as low as 0.5 mol % of $(Cu(I)OTf)_2 \cdot PhH$ and 1.0 mol % of 4,7-dichloro-1,10-phenanthroline as the ligand. Furthermore, cheap and stable copper precursors like Cu(I)I and $Cu(II)(OAc)_2 \cdot H_2O$ and the cheap and mild base K_2CO_3 can be used.

The synthesis of compounds bearing an arylated nitrogen moiety has gained widespread interest due to their key role in, for example, medically important species and in materials with useful interesting electronic and mechanical properties. Although several methods for the amination of aryl halides exist,[1] only a few are also applicable to the *N*-arylation of azaheterocycles[2–5] and the scope of the reaction is still limited. Therefore renewed interest in copper-catalyzed *N*-arylations of azaheterocycles has grown in recent years.[3] In addition, Buchwald has recently reported that the palladium- and copper-catalyzed coupling of 5-aminoindole with an aryl halide provides complementary products.[6] Moreover, as the cost of palladium is high, copper is more attractive for large-scale C–N coupling reactions.

The classical copper-catalyzed Ullmann coupling reaction[7] suffers from harsh reaction conditions, low to moderate yields, and the requirement of stoichiometric amounts of copper. Milder methods involving various arylating agents such as boronic acids, have appeared in the literature. It was shown that simple copper salts in protic solvents can efficiently couple aryl boronic acids with imidazole.[8] We recently reported a base-free and anaerobic modification of the Collman protocol[9] resulting in the efficient coupling of aryl boronic acids with imidazole and benzimidazole in the presence of binuclear bis-μ-hydroxy copper(II) complexes.[10]

Unfortunately, the scope of this Cu(II) catalyzed C–N coupling reaction is rather limited. Several other studies have focused on the use of aryl halides to arylate azaheterocycles.[11] Buchwald and co-workers reported the use of a copper(I)-catalyst for the *N*-arylation of azaheterocycles.[11g] This methodology employs copper(I) iodide and racemic *trans*-*N*,*N*′-dimethyl-1,2-cyclohexanediamine for the *N*-arylation of many azaheterocycles. Cristau et al. have shown that cuprous oxide in the presence of oxime ligands couple many azoles with aryl halides under mild conditions.[11j,k]

In a search for a more efficient and general method we report here our recent results in the field of copper-catalyzed *N*-arylation of azaheterocycles with aryl halides using various substituted 1,10-phenanthroline ligands.

For our initial screening studies we investigated the *N*-arylation of benzimidazole with 5-bromo-*m*-xylene in

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the presence of 5 mol % of $(Cu(I)OTf)_2$·PhH and 1.1 equiv of Cs_2CO_3 in NMP as solvent at 125 °C.

First, we investigated the effect of the presence of donor ligands on the outcome of the reaction. Monodentate and bidentate phosphorus ligands ($P(n\text{-}Bu)_3$, $P(C_6H_{11})_3$, $P(OPh)_3$, $P(o\text{-tolyl})_3$, PPh_3, dppe, dppf, and Xantphos) afforded low to moderate yields (results not shown). Therefore, we changed to chelating nitrogen ligands in the copper(I)-catalyzed *N*-arylation of benzimidazole. Since Buchwald had reported the efficient *N*-arylation of imidazoles using the 1,10-phenanthroline/$(Cu(I)OTf)_2$·PhH system,[5a] we focused on the use of similar ligands in the copper(I)-catalyzed *N*-arylation of benzimidazole with 5-bromo-*m*-xylene. Applying a variety of chelating 1,10-phenanthroline ligands (see Fig. 1) revealed a large ligand effect on the yield (Table 1). The parent 1,10-phenanthroline (**A**) afforded a moderate yield after 44 h. Substitution on the phenanthroline-ring (ligands **B**–**E**) gave a slight increase in the yield. Much to our surprise, 1,10-phenanthroline carrying two electron withdrawing chlorine groups (**F**) afforded excellent conversions; this system resulted in almost complete conversion (98%) after 44 h. The use of the more active 5-iodo-*m*-xylene as an aryl halide substrate resulted in 100% yield within 16 h. In none of the reactions were homo-coupled and dehalogenated products observed.

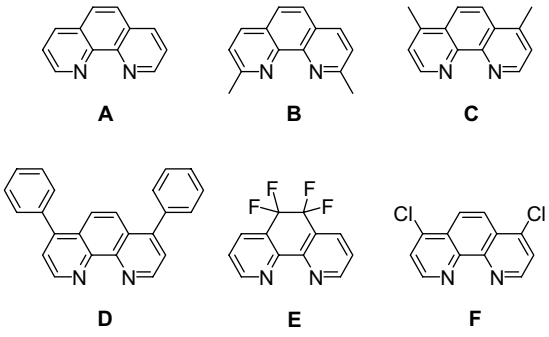
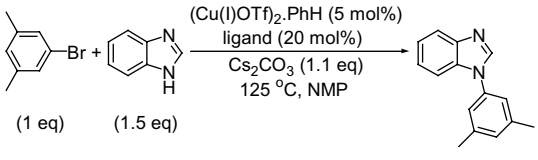


Figure 1. Substituted 1,10-phenanthroline ligands used in this study.

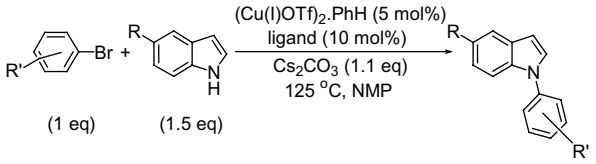
Table 1. *N*-Arylation using substituted 1,10-phenanthroline ligands[12]



Entry	Ligand[a]	% Conv. (22 h)	% Conv. (44 h)
1	**A**	12	43
2	**B**	17	50
3	**C**	14	54
4	**D**	26	60
5	**E**	24	64
6	**F**	79	98

[a] Ligands **E**[13] and **F**[14] were prepared according to literature procedures.

Table 2. *N*-Arylation of indole-derivatives[12]



Entry	ArBr	R	Ligand	% Conv. (h)	% Conv. (h)	% Conv. (h)
1	[a]	H	**A**	33 (17)	57 (41)	100 (113)
2	[a]	H	**F**	85 (17)	100 (89)	
3[b]	[a]	H	**F**	86 (17)	94 (41)	100 (113)
4	[a]	MeO	**F**	58 (17)	100 (89)	
5	[a]	CN	**A**	35 (17)	60 (89)	
6	[a]	CN	**F**	85 (17)	100 (89)	
7	[c]	H	**F**	100 (17)		
8	[d]	H	**A**	100 (17)		
9	[d]	H	**F**	80 (3)	100 (17)	

[a] Aryl bromide is 5-bromo-*m*-xylene.
[b] 1 equiv of the azole was taken.
[c] Aryl bromide is 4-bromopyridine.
[d] Aryl bromide is 5-bromopyrimidine.

Next, the scope of this *N*-arylation reaction was extended to other azaheterocycles and aryl halides. Table 2 shows that 5-bromo-*m*-xylene could be coupled to a variety of indoles using 5 mol % of $(Cu(I)OTf)_2$·PhH and 10 mol % of 4,7-dichloro-1,10-phenanthroline. The presence of a strong electron-donating substituent at the 5-position of the indole showed no significant effect on the yield (entry 4). Additionally, heteroaryl bromides like pyridines and pyrimidines were also converted quantitatively into C–N coupled products. In all cases, the reaction proceeded without the formation of side products.

Even though the described procedure is effective, all reactions showed the existence of an induction period. Since solubility of the catalyst seems to be the limiting factor we tried to improve the efficiency of the new $(Cu(I)OTf)_2$·PhH/4,7-dichloro-1,10-phenanthroline system. Only 0.5 mol % $(Cu(I)OTf)_2$·PhH and 1.0 mol % 4,7-dichloro-1,10-phenanthroline were premixed overnight at 125 °C before the reaction was initiated by the addition of Cs_2CO_3, the azaheterocycle and the aryl halide. Surprisingly, the *N*-arylation of benzimidazole with 5-iodo-*m*-xylene had already reached 100% conversion within 5 h (see Fig. 2). The use of 5-bromo-*m*-xylene under the same reaction conditions, using 1 mol % of copper-catalyst, afforded an 87% yield after 22 h.

We screened various copper precursors in the reaction of benzimidazole with 5-bromo-*m*-xylene (Table 3).

From Table 3 we can conclude that most Cu(I) salts give reasonable to high conversions after 22 h. Cu(I)I was almost as efficient as $(Cu(I)OTf)_2$·PhH in this *N*-arylation. Cu(I)I, however, is cheaper and more stable than $(Cu(I)OTf)_2$·PhH. The use of Cu(II) salts resulted in similar yields to those obtained with Cu(I) salts. The cheap $Cu(II)(OAc)_2$ salt afforded 98% conversion after 22 h. The presence of water did not influence the perfor-

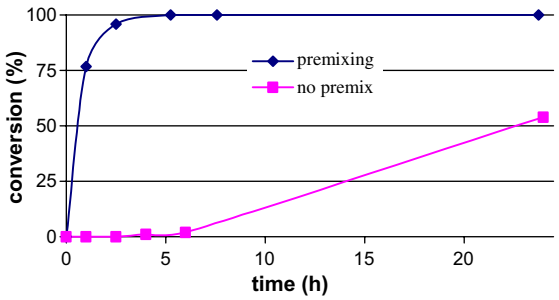
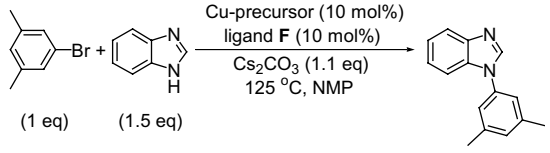


Figure 2. Premixing of ligand **F** in the presence of $(Cu(I)OTf)_2 \cdot PhH$ overnight before starting the reaction by addition of Cs_2CO_3, benzimidazole, and 5-iodo-*m*-xylene. The lines through the points are drawn for clarity.

Table 3. *N*-Arylation of benzimidazole with 5-bromo-*m*-xylene using various copper precursors[15]



Entry	Cu-precursor	% Conv. (22 h)	% Conv. (44 h)
1	Cu(0) powder (<200 mesh)	20	44
2	Cu(I)CN	22	48
3	Cu(I)Cl	62	99
4	Cu(I)Br	73	98
5	Cu(I)I	79	98
6	$(Cu(I)OTf)_2 \cdot PhH$[a]	100	
7	$Cu(II)Cl_2$	81	99
8	$Cu(II)Br_2$	70	94
9	$Cu(II)(OAc)_2$ anhydrous	98	100
10	$Cu(II)(OAc)_2 \cdot H_2O$	98	100

[a] 5 mol % of $(Cu(I)OTf)_2 \cdot PhH$.

mance of this catalytic system. Buchwald and co-workers also reported the successful use of several copper precursors in the arylation of *N*-methylformamide.[11b]

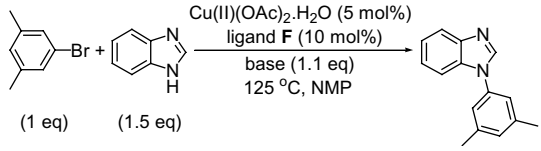
From these studies we conclude that relatively cheap and stable copper salts such as Cu(I)I and $Cu(II)(OAc)_2 \cdot H_2O$ can be used to arylate benzimidazole with aryl bromides in an efficient manner.

Since Cs_2CO_3 is a rather expensive base we tested the activity of a series of bases to make our methodology broadly applicable (Table 4).

The organic amine bases DABCO and triethylamine (entries 6 and 7) give low yields. The stronger inorganic bases (entries 1–4) all resulted in high conversions after 22 h. Similar results were obtained using Cu(I) iodide as a copper precursor. These studies have shown that the expensive Cs_2CO_3 can be replaced by the cheaper bases *t*-BuOK, K_2CO_3, and K_3PO_4.

We conducted the Cu(I)-catalyzed *N*-arylation of benzimidazole with 5-bromo-*m*-xylene using Cs_2CO_3 and

Table 4. *N*-Arylation of benzimidazole with $Cu(II)(OAc)_2 \cdot H_2O$ using a series of bases[15]



Entry	Base	% Conv. (22 h)
1	Cs_2CO_3	98
2	K_3PO_4	85
3	K_2CO_3	94
4	*t*-BuOK	99
5	NaOAc	5
6	DABCO	10
7	Et_3N	0

K_2CO_3 as bases at 80 and 125 °C (for reaction conditions see Table 3). At 125 °C, the conversions were 98% and 94% (22 h) using Cs_2CO_3 and K_2CO_3 as bases, respectively. At 80 °C, the same reaction profile was observed, although the reaction rate was somewhat lower. So, using Cs_2CO_3 and K_2CO_3 as bases afforded 63% and 57% conversion, respectively, after 54 h. Thus it is possible to conduct the *N*-arylation reaction at lower temperatures using the cheap and mild base K_2CO_3.

Another approach to lower the reaction temperature involves using a microwave. Microwave irradiation has become increasingly popular in recent years to improve the yield and to shorten reaction times in a variety of reactions.[16] Since microwave heating has also been successfully applied in several copper mediated *N*-arylation reactions,[17] we tested this methodology in the Cu(I)I/4,7-dichloro-1,10-phenanthroline catalyzed *N*-arylation of benzimidazole. The use of microwave irradiation resulted not in the formation of the desired product but in substitution of the chloro group of the ligand for a benzimidazole.[18] Even in the absence of Cu(I)I, this product was formed. We did not observe the formation of this coupling product when conventional heating was applied.

At present, the mechanism of Cu(I) catalyzed coupling reactions is still under debate.[19] For example, Buchwald proposed a catalytic cycle that starts with coordination of the amine, followed by oxidative addition of the aryl halide and then reductive elimination yielding the *N*-arylated compound and the catalytic copper-mediated species.[11b] Deng et al. reported that the oxidative addition of the aryl halide precedes coordination of the amine.[20] Recently, Cristau et al.[11k] ruled out the possibility of radical intermediates and proposed two alternative oxidative addition/reductive elimination mechanistic pathways. To the best of our knowledge, no mechanistic studies on the copper-catalyzed *N*-arylation resulting in the full elucidation of the catalytic pathway have been reported in the literature.

Figure 3 shows the reaction profile of the *N*-arylation of benzimidazole using the Cu(I)I/4,7-dichloro-1,10-phenanthroline catalyst. It was concluded that the presence

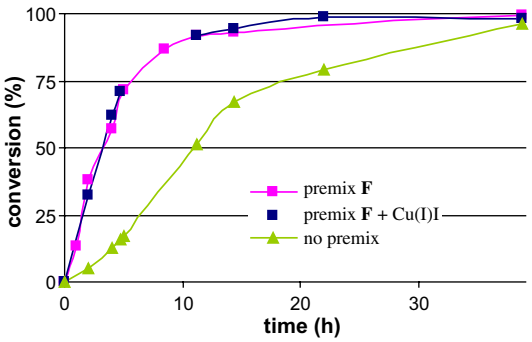


Figure 3. Premixing of ligand **F** in the presence and in the absence of Cu(I)I overnight before starting the reaction by addition of benzimidazole and 5-bromo-*m*-xylene. The lines through the points are drawn for clarity.

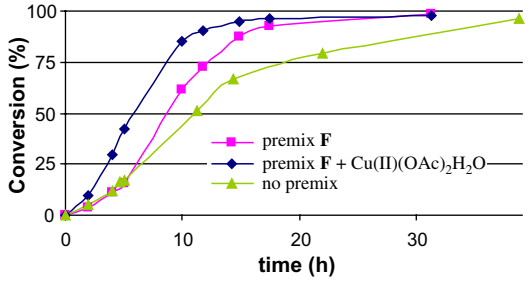


Figure 4. Premixing of ligand **F** in the presence and in the absence of $Cu(II)(OAc)_2{\cdot}H_2O$ overnight before starting the reaction by addition of benzimidazole and 5-bromo-*m*-xylene. The lines through the points are drawn for clarity.

of Cu(I)I during premixing did not affect the speed of the subsequent reaction. Premixing ligand **F** was sufficient to increase the reaction rate. In contrast, the presence of $Cu(II)(OAc)_2{\cdot}H_2O$ during premixing did affect the reaction profile (Fig. 4). If $Cu(II)(OAc)_2{\cdot}H_2O$ was present during premixing, the reaction rate increased. This may be an indication that the Cu(II) species was first reduced to Cu(I),[21] which is supposed to be the catalytic species.[22,23] Furthermore, the reaction must be performed under an inert atmosphere, since reaction under air did not result in product formation. Further studies are required for complete elucidation of the mechanism.

In summary, we have developed a highly efficient copper-catalyzed C–N coupling reaction of azaheterocycles with aryl halides using the chelating nitrogen ligand 4,7-dichloro-1,10-phenanthroline. The 4,7-dichloro-1,10-phenanthroline ligand gave superior conversions compared to the parent 1,10-phenanthroline. Aryl iodides, aryl bromides, and heteroaryl bromides can be coupled with a variety of azoles using this procedure. We have shown that the cheap and stable copper precursors Cu(I)I and $Cu(II)(OAc)_2{\cdot}H_2O$ can be used in this reaction. Furthermore, the cheap and mild base K_2CO_3 could be efficiently used. Predissolving the 4,7-dichloro-1,10-phenanthroline ligand increases initial reaction rates dramatically. When copper(II)-precursors are used, premixing the copper(II)-precursor together with the ligand leads to similar reaction rates as when using copper(I)-precursors. Preliminary mechanistic work is discussed and more detailed studies are in progress.

Acknowledgements

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12. Typical procedure for the *N*-arylation: A Schlenk vessel under nitrogen was loaded with $(Cu(I)OTf)_2{\cdot}PhH$ (25.3 mg, 5 mol %), the appropriate 1,10-phenanthroline ligand (10 or 20 mol %), Cs_2CO_3 (360 mg, 1.10 mmol), the appropriate aryl halide (1.00 mmol), the appropriate azaheterocycles (1.51 mmol), and dihexyl ether as an internal standard (118 μL, 0.502 mmol) in 0.67 mL of dry NMP. The reaction mixture was stirred under nitrogen at 125 °C. The conversion was verified by taking samples from the reaction mixture. CH_2Cl_2 and a saturated solution of NH_4Cl were added to the sample. After separation of the water layer, the organic layer was filtered through a plug of $MgSO_4$. The conversion and the selectivity of the reaction were determined by GC and GC/MS analysis.
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15. Typical procedure for premixing several reagents overnight at 125 °C before starting the *N*-arylation: A Schlenk vessel under nitrogen was loaded with the appropriate copper-precursor (10 mol %) and 4,7-dichloro-1,10-phenanthroline (24.9 mg, 10 mol %) in 0.67 mL of dry NMP. The reaction mixture was stirred under nitrogen overnight at 125 °C. The appropriate base (1.10 mmol), benzimidazole (178 mg, 1.51 mmol), 5-bromo-*m*-xylene (136 μL, 1.00 mmol) and dihexyl ether as an internal standard (118 μL, 0.502 mmol), were added to the reaction mixture, after which stirring was continued under nitrogen at 125 °C. The conversion was verified by taking samples (0.05 mL) from the reaction mixture. CH_2Cl_2 and a saturated solution of NH_4Cl were added to the sample. After separation of the water layer, the organic layer was filtered through a plug of $MgSO_4$. The conversion and the selectivity of the reaction were determined by GC and GC/MS analysis.
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