

## Diazabutadiene: a simple and efficient ligand for copper-catalyzed N-arylation of aromatic amines

Yu-Hua Liu,<sup>a,b</sup> Chen Chen<sup>a,b</sup> and Lian-Ming Yang<sup>a,\*</sup>

<sup>a</sup>Beijing National Laboratory for Molecular Sciences (BNLMS), New Materials Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>b</sup>Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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**Abstract**—Diazabutadienes (DABs) were chosen as ancillary ligands in the Cu-catalyzed C–N coupling reaction for the synthesis of triarylamines. A combination of CuI/DAB (**1**) [**1**: *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene] was found to be an efficient catalyst system for N-arylation of diarylamines and anilines with aryl iodides, affording the desired products in good to excellent yields.

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Triarylamine compounds are attractive targets for chemical synthesis because of their importance as building blocks of organic materials with electronic, photo-electronic and magnetic properties.<sup>1</sup> This has led to the development of many synthetic protocols using the transition metal-catalyzed C–N coupling. The most remarkable advances have been made in the Pd-catalyzed process, which can realize the coupling reaction of forming various C–N bonds under very mild conditions and becomes the most powerful tool for laboratory-scale preparation.<sup>2</sup> On the other hand, the Ullmann reaction,<sup>3</sup> a venerable method for the Cu-mediated C–N coupling, has also received a steady increase of interest. From a standpoint of large-scale or industrial preparation, Ullmann-type reactions are more preferred because copper catalysts have the advantages of cost savings, low toxicity, and air- and moisture-stability. Recently, much work has been done to overcome the inborn drawbacks (harsh reaction conditions, requirement for large amounts of copper agents, and moderate yields) of the conventional Ullmann reaction, and proved that the activity of copper catalysts could be greatly improved by the use of proper ligands.<sup>4</sup> The more practical ligand-promoted Cu-catalyzed chemistry (so-called post-Ullmann reactions) is being developed, and various types of ligands, such as aliphatic diamines, 8-hydroxyquinoline, phosphines, ethylene glycol, glycine and proline, have been employed.<sup>4</sup> With regard to the synthesis

of triarylamines by the ligand-promoted Cu-catalyzed coupling, some successful examples involved the use of Cu(I)/phenanthroline system,<sup>5</sup> Cu(I)-neocuproine complex,<sup>6</sup> CuI/N- or P-based bidentate ligand systems,<sup>7</sup> CuI/P(Bu)<sub>3</sub> system,<sup>8</sup> CuI/pyridine-based systems,<sup>9</sup> as well as Cu(I)-phenanthroline complexes.<sup>6,10</sup>

As part of our research, we are interested in the exploration of other efficient ligands, but simple and inexpensive, for the copper-catalyzed synthesis of triarylamines. We notice a known family of ligands with the chelating nature, 1,4-diazabuta-1,3-dienes (DABs). DABs are readily available from the condensation of glyoxal with primary amines, and conveniently manipulated due to their insensitivity to air or moisture. Their coordination versatility stems from the flexibility of the N=C–C=N backbone and the strong  $\sigma$ -donating and  $\pi$ -accepting properties. The steric factors of DABs can be easily modulated by the change of groups on the amine section of DAB. These features of DABs would be favorable for stabilizing catalytic species and assisting catalytic cycle. Their coordination capability was well documented in the DAB–metal complexes,<sup>11</sup> but they were rarely used as additive ligands in the catalytic coupling reaction.<sup>12,13</sup> Here, we wish to report our preliminary investigation in the employment of DABs as ancillary ligands in Cu-catalyzed N-arylation of aromatic amines for the synthesis of triarylamines.

With DABs as ligand, a set of experiments was carried out to optimize the reaction conditions. We determined

\* Corresponding author. E-mail: [yanglm@iccas.ac.cn](mailto:yanglm@iccas.ac.cn)

KO<sup>t</sup>Bu as the base of choice, toluene as the solvent of choice, and the catalytic system composed of 1.2:1 molar ratio of DAB to Cu. The N-arylation of diphenylamine with iodobenzene in the presence of 5 mol % CuI and 6 mol % of DAB (**1**) [**1**: *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene] proceeded at 120 °C to give an excellent isolated yield (Table 1, entry 2). The role of DAB (**1**) was confirmed by running a control experiment (Table 1, entry 1). The use of other several diazabutadienes led to the observation that aryl-diazabutadienes are superior to alkyl-diazabutadienes (Table 1, entries 2 and 3 vs entries 4 and 5) as ligands for this Cu-catalyzed N-phenylation. This reactivity trend could result from the fact that there exists a better balance between the electronic and steric effects in the aryl-DAB. It was shown that the aryl-DAB has a comparable performance to the commercially available ligands phenanthrolines<sup>5,6</sup> and 2,2'-bipyridyl.<sup>4c,7</sup>

With the optimum conditions in hand, we checked the reactivity of a few diarylamines and some un-activated aryl iodides (Table 2). In most cases, this protocol afforded the desired products in good to excellent yields (entries 1–5, 7, and 9–11). The iodide with electron-donating substituents led to the reduced yields (entries 2, 3, 5, and 6). For diarylamines, the effect of the steric factor on this reaction appeared to be greater than that of the electronic factor. For instance, the reaction of di(*p*-tolyl)amine gave comparable yields to that of diphenylamine (comparing entries 1–3 with entries 4–6), while the sterically hindered (1-naphthyl)phenylamine reacted with iodobenzene to afford a far lower yield than

the less hindered (2-naphthyl)phenylamine (entry 7 vs 8). For aryl iodides, the one with the *p*-methoxy group gave the decreased yields compared to that with the *p*-methyl group (entry 3 vs 2; and entry 6 vs 5). Additionally, the double amination proceeded smoothly under similar conditions when diiodobiphenyl was treated with

**Table 2.** N-arylation of diarylamines catalyzed by the CuI/DAB (**1**) system

Entry	Amine	Aryl halide	Yield <sup>a</sup> (%)
1			94
2			79
3			72
4			88
5			87
6			63
7			88
8			38
9			85 <sup>b</sup>
10			83 <sup>b</sup>
11			87 <sup>b</sup>

**Table 1.** CuI-catalyzed N-phenylation of iodobenzene using different DABs as ligand

Entry	Ligand	Yield <sup>a</sup> (%)
1	No ligand	67
2		94
3		90
4		64
5		75

Reaction conditions: aryl halide: 1.25 mmol; diarylamine: 1 mmol; CuI: 5 mol %; DAB ligand: 6 mol; KO<sup>t</sup>Bu: 1.5 mmol; solvent: toluene, 5 mL; temperature: 120 °C; reaction time: 20 h.

<sup>a</sup> Isolated yields.

Reaction conditions: aryl amine: 1.0 mmol; aryl halide: 1.25 mmol; CuI: 5 mol %; DAB (**1**): 6 mol %; KO<sup>t</sup>Bu: 1.5 mmol; toluene: 5 mL; reaction temperature: 120 °C; reaction time: 20 h.

<sup>a</sup> Isolated yields.

<sup>b</sup> Molar ratio of amine to halide: 2.5:1.

**Table 3.** N-diarylation of anilines catalyzed by the CuI/DAB (**1**) system

Entry	Amine	Aryl halide	Yield <sup>a</sup> (%)
1			97
2			92
3			82
4			82
5			84
6			73
7			76
8			75

Reaction conditions: aryl iodide: 4.0 mmol; aryl amine: 1.0 mmol; CuI: 5 mol%; DAB (**1**): 6 mol%; KO<sup>t</sup>Bu: 3 mmol; toluene: 5 mL; reaction time 48 h; reaction temperature: 120 °C.

<sup>a</sup> Isolated yields.

diarylamines (entries 9–11). In this reaction, the side reaction was the homocoupling of the aryl iodide to form biaryls.

We also found that the CuI/DAB (**1**) system was effective for the coupling reaction of primary arylamines with aryl iodides, and N-diarylation proceeded in good to excellent yields as shown in Table 3. The use of larger excess of aryl iodides was favorable for avoiding the formation of a mixture of triarylamine and diarylamine. The experiment demonstrated that 3 equiv of iodobenzene was coupled with 1 equiv of diphenylamine to give only an 80% yield of triphenylamine (compare entry 1 in Table 3). Anilines with *p*- and *m*-methyl or *p*-methoxy group are all viable coupling partners in this reaction (Table 3, entries 3–8).

In summary, a simple and efficient method for Cu-catalyzed N-arylation of diarylamines and anilines has been developed based on CuI/DAB systems. This CuI/DAB (**1**) catalytic system represents an interesting alternative to the existing copper catalytic systems. Further effort is directed at extending the scope of electrophilic substrates used in the CuI/DAB catalytic systems from aryl iodides to aryl bromides or even chlorides, and studying the influence of the steric and electronic factors of DAB

ligands on the coupling reactions. This work is ongoing in our laboratory.

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### Supplementary data

Detailed experimental procedure and characterization of the products. This material is available free of charge. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.103.

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