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## Cp\*Co(III) and Cu(OAc)<sub>2</sub> Bimetallic Catalyst for Buchwald type C-N Cross Coupling of Arylchlorides and Amines under Base, Inert gas & Solvent-free Conditions

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This article is dedicated to the 65<sup>th</sup> birth anniversary of Professor Pradeep Mathur, IIT Bombay, India.

A bimetallic catalytic strategy in the combination of Cp\*Co(CO)I<sub>2</sub> and Cu(OAc)<sub>2</sub> is used for Buchwald type C-N coupling reaction of aryl chlorides and amines. The reaction works at 100 °C to produce an excellent yield of the desired C-N coupling product, in 4 h, under aerobic reaction conditions. The reactions run under base free and solvent-free conditions, which enables this strategy to work efficiently for electron-withdrawing and base sensitive functionalities. The presented methodology is found to be equally efficient for electron-donating functionalities as well as for the primary 1° and 2° aromatic and aliphatic amines. Moreover, the products can be easily separated through the extractions of the organic aqueous layer, and this process does not demand chromatographic separations.

3d-Transition metal catalysts have produced vast opportunities to perform commercially important reactions economically. In recent years, the non-noble metals such as cobalt and copper had marked their presence in catalysis through their applications in various catalytic reactions.<sup>1-3</sup> Since the pioneering work of Ullmann<sup>4a</sup>, 1901 and Kharasch<sup>4b</sup>, 1941 using Cu and Co catalysed aryl homocoupling reactions, these metals had received remarkable attention for various coupling reactions. Moreover, the increasingly attractive, distinctive catalytic and additionally being inexpensive due to abundance makes these elements more desirable alternative over the precious metal catalysts.

Presence of heteroatom and strategic position of a carbonheteroatom bond is quite crucial to enhance the activity and various other applications.<sup>5</sup> The year 2019 is the silver jubilee of the Buchwald-Hartwig coupling reaction, indeed, it is one of the outstanding discovery which enables us to synthesize a large variety of C-N coupling products with ease from last two decades.<sup>6-9</sup> Recently, the bimetallic catalytic strategies became an alternate paradigm to perform C-C coupling reactions.<sup>10</sup> But, the bimetallic strategies are rarely known for the heteroatom cross-coupling reactions like C-N bond formations.

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The single-site approaches include the Buchwald-Hartwig coupling<sup>11</sup> with Pd metal, and various other metal-based approaches have been employed for C-N coupling reactions.8 Apart from that, a variety of Cu compounds has been used for the Ullmann type coupling reactions.<sup>12</sup> However, most of the reactions, utilise strong base, most commonly <sup>t</sup>BuONa or <sup>t</sup>BuOK and organic solvents. The use of a strong base in a polar aprotic or non-polar solvent is not advisable due to their low solubility, which directly increases the time of reaction. Also, the use of a strong base with aryl halides leads to the formation of Na or K salts as a by-product.<sup>13</sup> The low solubility of Na or K salts triggers the precipitation, hence, discouraged to use in flow reactors for bulk synthesis.13 Furthermore, the use of a strong base in the reaction restricts its application towards base sensitive functionalities. The Ullmann type C-N coupling reactions, are considered as an economical alternate but, the stoichiometric amounts of Cu, long reaction time, high temperature, presence of a base and limited substrate scope are some of the associated drawbacks.<sup>7</sup> Scheme 1 shows the earlier methods of amination, the classical methodologies are multistep and less efficient, Ullman and Chan-Lam coupling reaction require a long time,14 while the Buchwald-Hartwig coupling is the latest upgrade in this series, which need Pd catalyst, base and solvent.7,15 Metal carbonyl complexes are well-known for various catalytic reactions.<sup>16-18</sup> The high valent [Cp\*Co(CO)I<sub>2</sub>] complex is well established<sup>19</sup> for C-C coupling reactions via C-H activation.<sup>20-21</sup> In recent, Matsunaga and coworkers used Cp\*Co(III) for amidations of thioamide,<sup>21</sup> moreover, the o-amidations of benzaldehyde has also been reported by Sundararaju and co-workers.<sup>22</sup>

Herein, we report  $Cp^*Co(CO)I_2$  and  $Cu(OAc)_2$  as an efficient bimetallic catalyst for Buchwald type C-N reaction. The method works under the aerobic, solvent and base free condition to produces exceptional yields in just 4h. Moreover, the method is also found suitable for base sensitive functional groups and show wide functional group tolerance. To the best of our knowledge, this the first report where the Cp\*Co(III) has been exploited for the CN bond formation between aryl chloride and amines.

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<sup>+</sup> Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x







Scheme 2. Co and Cu co-catalysed C-N coupling reaction

In 2008 Lipshutz et al., used Ni/Cu@C with tert-BuOLi as a heterogeneous bimetallic catalyst at 200 °C for C-N coupling reactions.<sup>23</sup> Recently we had also reported a pyrazolated chalcogenide (n<sup>5</sup>-Cp\*)Rh(III) catalyst for the base and solventfree C-N coupling under aerobic conditions.<sup>24</sup> Despite of exceptional catalytic activity of the complex, Rh is an expensive metal. Hence, to find an alternate, an experiment was executed with chlorobenzene and pyrrolidine in presence of Cp\*Co(CO)I<sub>2</sub> and Cu(OAc)<sub>2</sub> at 100 °C for 6 h in solvent and base free conditions. The initial reaction worked very well and resulted in 92% yield of desired C-N coupling product (Scheme 2). To explore the necessary insights of the reaction, the mixture of pyrrolidine and chlorobenzene was heated with a 10 mol% of Cu(OAc)<sub>2</sub> and in absence of Cp\*Co(III), the yield of desire product was drastically reduced and it took more than 36h to give 38% transformations (Table 1, Entry 1). In contrast, the Cp\*Co(III) failed to mimic the reaction in the absence of Cu(OAc)<sub>2</sub> (Table 1, Entry 2). The reaction produces a maximum transformation (93%) when a mixture of Cp\*Co(III) (1 mol%) catalyst and Cu(OAc)<sub>2</sub> (10 mol%) was considered (Table 1, Entry 3). Reducing the quantity of Cu(OAc)<sub>2</sub> significantly reduced the present transformation, as 54, 38 and 31% coupling product was obtained with 5, 2 and 1 mol% of Cu(OAc)<sub>2</sub> respectively, (Table 1, Entry 4-6). Moreover, reducing the quantity of the Cp\*Co(CO)I<sub>2</sub> from 1 mol% to 0.25 mol% severely affects the yield of the product (Table 1, Entry 7 and 8). The continuous reaction monitoring up to 24 h at 0.5 mol% and 0.25 mol% catalyst loading shows the average yield of 45% and 38% respectively, the prolong heating also failed to scale up the transformations and resulted in the decomposition of catalyst. Further optimisation of the identified reaction encompasses the scope of other Copper salts, CuCl<sub>2</sub>, CuSO<sub>4</sub> and Cul but, no catalytic activity was detected (Table 1, Entry 9-11). During the temperature optimizations, 100 °C was found to be efficient for the reaction, hence, most of the reactions were performed at 100 °C.

The performing reaction at low temperature acutely affects the product yield. Dropping the reaction temperature to 80 °C in a duration of 4 h reduces the product yield to 55% (Table 1, Entry 14). While further reducing the reaction temperature to 60 °C, drops down the product yield close to the  $1/3^{rd}$  of the actually obtained yield (Table 1, Entry 13). No product formations were detected when the reaction was performed at room temperature (Table 1, Entry 12). While optimizing the reaction time, it was experienced that a traceable quantity of product was formed in the initial hour of the reaction which keeps on increasing gradually in subsequent hours.

#### **Table 1**. Optimisation of various reactions parameters

S.No	Co(III) Cat.	Cu(OAc) <sub>2</sub>	Temp	Time	Yield <sup>a</sup>
	mol%	mol%	[°C]	[h]	%
1.		10	100	36	36
2.	1		100	24	
3.	1	10	100	4	93
4.	1	1 <sup>b</sup>	100	4	31
5.	1	2	100	4	38
6.	1	5	100	4	54
7.	0.5 <sup>b</sup>	10	100	24	45
8.	0.25 <sup>b</sup>	10	100	24	38
9.	1	10 (CuCl <sub>2</sub> )	100	8	
10.	1	10 (CuSO <sub>4</sub> )	100	8	
11.	1	10 (Cul)	100	8	
12.	1	10	RT	12	
13.	1	10	60	4	28
14.	1	10	80	4	55
15.	1	10	100	1	20
16.	1	10	100	2	48
17.	1	10	100	3	76

<sup>a</sup>Isolated Yields, <sup>b</sup>gram scale reaction, Pyrrolidine (1mmol), Chlorobenzene (1mmol)

Using the optimized conditions, the substrate scope of the reaction was explored, it was started with aliphatic amines (Table 2, 1a - 1k) which includes cyclic aliphatic amines, aliphatic primary and secondary amines. In general, the significant transformation was observed with the electron-withdrawing functionalities as compared to donor groups. The presence of withdrawing group at the *ortho*- position shows a slight decrease in the product yield.

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1j, 78%

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**Table 2.** Substrate Scope of reaction aliphatic amines and arylchlorides

1k, 71%

The very first reaction while exploring the substrate scope was the chlorobenzene and pyrrolidine which exceptionally yields 91% (1a). The coupling of para-nitrochlorobenzene and paratriflouromethylchlorobenzene with pyrrolidine shows the sizeable transformation of 82% (1b) and 87% (1c) respectively. Similar reactions when repeated with piperidine produces the desire products with the marginal deviation compared to pyrrolidine, 83% (1d) and 89% (1e) yields were recorded respectively. The substantial transformation was observed with the ortho- substitutions. The reactions of 2nitrochlorobenzene with pyrrolidine and piperidine yields 80% (1f) and 82% (1g) coupling products. Further reactions of paraand meta- substitutions of methylchlorobenzene and pyrrolidine show a slight decrease in the yield. The paramethylchlorobenzene produces 75% (1h) yield, while reaction with 3-methylchlorobenzene shows further decrease and 67% (1i) of the desired transformation was obtained. Apart from that, reactions with diethylamine (a non-cyclic aliphatic amine) and para-nitrochlorobenzene produce 78% (1j), while propyl amine and para-cyanochlorobenzene produced 71% (1k) transformation to the desired coupling product.

Furthermore, the substrate scope was extended to benzylic amine and excellent results were obtained in most of the reactions (Table 3). The excellent yield of 89% (2a) was afforded in the reaction of benzyl amine and chlorobenzene. Electron withdrawing groups such as  $NO_2$ ,  $CF_3$  and C-N were found to be well tolerated. The reactions of *para*-nitro, *para*-

triflouromethyl and para-cyano-chlorobenzenes, with benzyl amine yields of 86% (2b), 90% (2c) and 89% (2d), 405 pectively. A slightly decreased yield was recorded when benzyl amine was reacted with para-methylchlorobenzene, it produces 83% (2e) yield of the desired product. The further loss in the transformation was observed during the reaction of 2nitrochlorobenzene and benzylamine, 69% (2f), presumably steric hindrances and electronic interactions are the possible factors. Furthermore, heterocyclic substrates were also explored and the significant transformation was obtained, the 2-chloropyridine reacts well with benzyl amine to yield 77% (2g) of the product. The Para-methyl substitution over benzylamine shows a slightly less transformation 73% (2i), while, an appreciable transformation of 76% (2h) was recorded for para-nitrochlorobenzene and 2-chloropyridine coupling product.

Table 3. Scope of reaction for benzylamine and arylchlorides



Reaction *conditions*: Amines (1mmol), arylhalide (1mmol),  $Cp*Co(CO)I_2$  (1 mol%),  $Cu(OAc)_2$  (10 mol%), 100 °C, 4 h.

The scope of the reaction was also investigated for aromatic amines (Table 4). The reaction of aniline with chlorobenzene was found to be quite efficient, and a 86% (3a) yield was afforded from the reaction. *Para*-nitro and paratriflouromethylchlorobenzenes produce excellent yields of 88% (3b) and 85% (3c) respectively. The reaction of paramethylchlorobenzene and para-methoxychlorobenzene affords 73% (3d) and 80% (3e) yield respectively. 2-Chloropyridine and aniline exhibited а considerable 76% transformation of (3f). 2-Nitro and 2methylchlorobenzene reacts with aniline to produces 70% (3g) and 68% (3h) of corresponding amine products. Halide substituted anilines and other withdrawing functionalities like NO<sub>2</sub> (ortho- and para-) failed to transform the desire products. However, the donor group functionalised aniline were identified as active substrates for the coupling reaction. Paramethylaniline and para-methoxyaniline produces 67% (3i) and 72% (3j) yield of their respective coupling products

Reaction conditions: Amines (1mmol), Arylcholoride (1mmol), Cp\*Co(CO)I<sub>2</sub> (1 mol%), Cu(OAc)<sub>2</sub> (10 mol%), 100 °C, 4 h.

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3i, 67%

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respectively. 2-methylaniline also produces 63% (3k) yield of desire coupling product.

**Table 4**. Scope reaction of anilines and aryl chlorides

$$R \stackrel{\text{NH}_2}{\longleftarrow} + R_1 \stackrel{\text{Cl}}{\longleftarrow} X \stackrel{\text{Cp*Co(CO)}_2 (1 \text{ mol}\%)}{100 \text{ °C}, 4 \text{ h}} R \stackrel{\text{H}}{\longleftarrow} R \stackrel{\text{X}}{\longleftarrow} R_1$$
  
R = H, Me, OMe R<sub>1</sub> = H, EWG, Me, OMe  
X = CH N

Reactions of substituted arylchlorides and aniline



Reaction conditions: Amine (1mmol), Arylhalide (1mmol), Cp\*Co(CO)I<sub>2</sub> (1 mol%), Cu(OAc)<sub>2</sub> (10 mol%), 100 °C, 4 h,

3j, 72%

3k, 63%

To study the selectivity trend of present coupling towards varies amines and arylhalides, some intermolecular competitive experiments were performed. A reaction of *para*-nitrochloro benzene and *para*-methylchlorobenzene with pyrrolidine shows a complete selectivity towards the electron-withdrawing functionality. These results indicate the faster coupling of the reaction for electron-withdrawing functionalized aryl halide.



**Scheme 3**. A competitive reaction of pyrrolidine with a mixture of p-nitrochlorobenzene and p-methylchlorobenzene



**Scheme 4**. competitive reaction of 1° amines (aromatic and aliphatic) with chlorobenzene

Several other control experiments justifying the selectivity towards various amines are also performed. A reaction using a mixture of propylamine and aniline with chlorobenzene exclusively produces the diphenylamine (Scheme, 4), Another reaction using a mixture of benzylamine 1846998016628466 chlorobenzene produces a comparative yield in the ratio of 1.4: 1. The reaction between benzyl amine and chlorobenzene was dominant (Scheme 5).



Scheme 5. Competitive reaction of 1° amines & chlorobenzene

Another competitive trail includes a comparison between primary and secondary aliphatic amines. In this trial, two individual reactions of chlorobenzene, one with propylamine and pyrrolidine (scheme 6), and another with propylamine and diethylamine (Scheme 6 and 7) were studied. In both reactions, coupling was dominated with secondary amine.



Scheme 6. Competitive reaction of 1° and 2° aliphatic amines



Scheme 7. Competitive reaction of 1° and 2° aliphatic amines

Furthermore, comparing the secondary aliphatic amines (cyclic and acyclic amines, produces the product with only with cyclic amine (Scheme 8). Also, the experiments comparing secondary aromatic amine i.e. diphenylamine with pyrrolidine and diethylamine yield products only with aliphatic amines (Scheme 9).



Scheme 8. Competitive reaction of 2° amines & chlorobenzene



Scheme 9. competitive reaction of 2° amines & chlorobenzene

Based on the literature evidences, a plausible mechanism is drawn (Scheme 10). Probably, the catalytic cycle initiates with the reduction of  $Cp^*Co(III)$  complex (1) to  $Cp^*Co(I)$  intermediate (2). However, the source of this reduction

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process is not confirmed, but it might be probably obtained by the reduction of cationic intermediate<sup>25</sup> [Cp\*CoOAc]<sup>+</sup>, which can be formed by the interaction of 1 and Cu(OAc)<sub>2</sub>. However, there is possibility that amine may be involve in this reduction process.<sup>26</sup> Intermediate (2) undergoes oxidative addition with arylchloride to give adduct (3). This interact with amine and produce an intermediate (4) and eliminate an ammonium salt, formed by interactions of HCl and available amine. Intermediate (4) undergoes reductive elimination and ultimately produces the desired product and regenerates the Cp\*Co(I) complex for the next catalytic cycle.

Scheme 10. The plausible mechanism for the catalytic reaction

### Conclusions

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A bimetallic catalytic system consisting of  $Cp*Co(CO)I_2$  and  $Cu(OAc)_2$  complexes catalytically coupled the aryl chloride and amines and established a strongly feasible strategy for the C-N coupling reactions. The present method demands very less amount of inexpensive Co and Cu metal catalyst and works efficiently in base free and solvent-free conditions. The present strategy is also found to be highly suitable for the primary and secondary aliphatic amines, benzylic amines and aniline. Moreover, the reaction has a bit advantages for the electron-withdrawing functionalized aryl halides, moreover, this is the first report of Cp\*Co(III) catalysed cross-coupling of aryl chloride and amines.

## **Conflicts of interest**

"There are no conflicts to declare".

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