### **RESEARCH ARTICLE**



WILEY Heteroatom Chemistry

## Cu(II) complex of phenylthiosemicarbazone: An in situ catalyst for formation of C-N bond between different N-based neucleophiles with arylboronic acids at room temperature

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### Abstract

We have reported here a new synthetic protocol for the formation of C-N bond catalyzed by a thiosemicarbazone complex of copper. This in situ complex has been found to be very effective for Chan-Lam C-N cross-coupling reaction of anilines and various imidazoles at room temperature. Pyrazole and 4-bromoindole were also activated for C-N bond formation by using this protocol at room temperature. This catalytic system gave good-to-excellent yield using a mixture of DMF and water as solvent in a 1:1 proportion.

### **1** | INTRODUCTION

Transition metals such as Pd- and Cu-mediated C-N bond formation can be categorized into three distinct different types, (a) regular cross-coupling, (b) oxidative cross-coupling, and (c) inverse or Umpolung cross-coupling. All these three types of cross-coupling can be performed effectively with the help of catalysts containing palladium and copper.<sup>[1]</sup> As initially reported by Chan and Lam, copper-mediated cross-coupling of arylboronic acids and nitrogen-based nucleophiles is an important strategy for C-N bond formation.<sup>[2]</sup> From their report, it is evident that the N-arylation of nitrogen-based nucleophiles by arylboronic acids can be carried out with the help of stoichiometric amount of Cu salt in presence of an external base/ligand. This methodology is very efficient with a wide range of substrate variety and applicable both in the liquid phase and on solid support. It has several advantages including mild reaction conditions, use of weak bases, low toxicity, high thermal stability, and structural diversity of arylboronic acid over the use of aryl halides and thus makes this process better than the classical Ullmann coupling<sup>[3]</sup> reaction and Pdcatalyzed Buchwald-Hartwig amination.<sup>[4]</sup> Recently, this has been modified by the use of various additives, such as 2,2 ,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), pyridine-Noxide, and molecular oxygen.<sup>[5]</sup> Some other works involving coupling reactions of imidazoles with arylboronic acid have been reported by various workers, for example synthesis of Cu(II)-tetramethylethylene diamine complex by Collman et al, synthesis of Cu(II)-salen type complex by Bora et al, and synthesis of chitosan anchored copper(II) Schiff base complexes by Anuradha et al<sup>[6]</sup> are significant. Similarly, Azam et al<sup>[7]</sup> also reported a new Cu(II) salen complex with propylene linkage for C-N bond formation between arylboronic acid and various N-heterocycles. To the best of our knowledge, there is no report on the use of Cu catalysts bearing thiosemicarbazone ligands in Chan-Lam cross-coupling reactions. The derivatives of thiosemicarbazone possess several characteristics such as (i) they can act as N,S donors and can form useful transition metal complexes having industrial applications,<sup>[8]</sup> (ii) they are also capable of acting as bi-or multidentate ligands through several donor atoms, (iii) the most important characteristics of these ligands are their capability of occupying different coordination sites available on the metal and thereby control the mode of coordination of the substrates with the metal influencing the selectivity and efficiency of the catalyst.<sup>[9]</sup> These characteristics of thiosemicarbazone make them suitable in the synthetic and catalysis

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chemistry involving transition metal complex formation.<sup>[10]</sup> In this communication, we wish to report a new protocol for Chan-Lam cross-coupling reaction using Cu thiosemicarbazone complex in a DMF:H<sub>2</sub>O (1:1) mixed solvent at room temperature.

#### Characterization of ligand (L) and 1.1 complex (C)

The m/z value of the ligand was found to be 316:  $[M + 1]^+$ .

#### 1.2 **FT-IR study**

In the FT-IR spectrum of L (Figure 1), the peaks observed at 1630, 2845, and 850 cm<sup>-1</sup> are assigned to the  $v_{C=N}$ ,  $v_{O-CH3}$ , and  $v_{C=8}$ , respectively. Peak at 3324 cm<sup>-1</sup> corresponds to  $v_{N-H}$  stretching and a peak at 1150 cm<sup>-1</sup> is due to  $v_{N-N}$ stretching (Figure 2).<sup>[11]</sup>

### **1.3** | <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral analysis of the ligand

### 1.3.1 | L:<sup>1</sup>H NMR [400 MHz, DMSO-d<sub>6</sub>, δ ppm]

 $N^{2}H$ : 9.80 (s, 1H), HC=N: 8.30 (s, 1H),  $N^{4}H$ : 9.45 (s, 1H), Ph<sup>a</sup>H: 6.96-7.22 (m, 3H), Ph<sup>b</sup>H: 7.35-7.84 (m, 5H), CH<sub>3</sub>: 3.55, 3.81 (2S, 6H) (Figure S1).

### L:<sup>13</sup>C-NMR [100 MHz, DMSO-d<sub>6</sub>, δ 1.3.2 ppm]

57 (C<sup>6</sup>-H<sub>3</sub>), 56 (OCH<sub>3</sub>), 139.7, 129.3, 123.6, 118.6, 126.7, 126.5, 118.2, 114.2, 111.4 (Ph C), 154.1 (C-N<sup>1</sup>), 177 (C-S) 154.8 (C-N<sup>4</sup>H) (Figure S2).

#### 1.4 **FT-IR spectrum of complex**

In the FT-IR spectrum of complex C (Figure 3), peaks appears at 3087 and 2998  $\mbox{cm}^{-1}$  corresponds to  $v_{N\ -H}^{\ 2}$  and  $v_{N\ -H}^{\ 4}$  . The weak peaks at 2830, 823, and  $1614 \text{ cm}^{-1}$  are due to  $v_{\text{O-CH3}}, v_{\text{C=S}},$  and  $v_{\text{C=N}},$  respectively. A peak at 1174  $\text{cm}^{-1}$  is due to v<sub>N-N</sub> stretching.<sup>[11]</sup>









FIGURE 2 Numbering of atom position in L



FIGURE 3 FT-IR spectrum of the complex (C)

### **1.5** | ESR and electronic spectra of the complex

From the ESR spectrum of the complex (Figure 4), it was clear that Cu is present in +2 oxidation state in the complex with g value 2.0073. In the electronic spectrum of Cu complex, the appearance of an absorption band at 352 nm is indicative of

2 of 10







# **TABLE 1**Screening and controlexperiment for Chan-Lam reaction<sup>a</sup>

|       | NH <sub>2</sub> B(OH) <sub>2</sub><br>+ Catalyst<br>Solvent, Base |           |         |      |          |              |
|-------|---|-----------|---------|------|----------|--------------|
| Entry | Ligand  | Cu source | Solvent | Base | Time (h) | %Yield       |
| 1     | _   | -         | +       | +    | 5        | NR           |
| 2     | +   | -         | +       | +    | 5        | NR           |
| 3     | +   | -         | +       | _    | 5        | NR           |
| 4     | _   | +         | -       | _    | 5        | Trace amount |
| 5     | _   | +         | +       | +    | 5        | Trace amount |

<sup>a</sup>Reaction condition: phenyl boronic acid (1 mmol), aniline (0.5 mmol), solvent (3 mL) in air; NR; no reaction.

## 4 of 10 WILEY Heteroatom Chemistry

|       | $H_2 = B(OH)_2$ $+ \bigcup = \frac{Cu\text{-source (mol)}}{H_2O(3ml), Et_3N(2e)}$ | %)<br>quiv.) | $\bigcirc$          |
|-------|---|--------------|---------------------|
| Entry | Cu source (mol %)   | Time (h)     | %Yield <sup>a</sup> |
| 1     | $Cu(OAc)_2 \cdot H_2O$ (10)   | 14           | 38                  |
| 2     | $CuSO_4 \cdot 5H_2O(10)$  | 14           | 35                  |
| 3     | $CuCl_2 \cdot 2H_2O(10)$  | 14           | 35                  |
| 4     | $Cu(OAc)_2 \cdot H_2O(10) + L(10)$  | 14           | 95                  |
| 5     | $CuCl_2 \cdot 2H_2O(10) + L(10)$  | 14           | 92                  |
| 6     | <b>C</b> (10)   | 14           | 90                  |

<sup>a</sup>isolated Yield.

|       | NH <sub>2</sub> B(OH) <sub>2</sub>         | Catalyst<br>Solvent, Base       | NH       |                     |
|-------|--|---------------------------------|----------|---------------------|
| Entry | Solvent                                    | Base (equiv.)                   | Time (h) | %Yield <sup>b</sup> |
| 1     | H <sub>2</sub> O                           | Et <sub>3</sub> N               | 14       | 85                  |
| 2     | CH <sub>3</sub> CN                         | Et <sub>3</sub> N               | 14       | 75                  |
| 3     | <sup>i</sup> PrOH                          | Et <sub>3</sub> N               | 14       | 67                  |
| 4     | DMF  | Et <sub>3</sub> N               | 14       | 89                  |
| 5     | МеОН                                       | Et <sub>3</sub> N               | 14       | 75                  |
| 6     | CH <sub>3</sub> CN:H <sub>2</sub> O        | Et <sub>3</sub> N               | 14       | 70                  |
| 7     | H <sub>2</sub> O: <sup><i>i</i></sup> PrOH | Et <sub>3</sub> N               | 14       | 68                  |
| 8     | DMF:H <sub>2</sub> O                       | Et <sub>3</sub> N               | 14       | 95                  |
| 9     | DMF:H <sub>2</sub> O                       | K <sub>2</sub> CO <sub>3</sub>  | 14       | 59                  |
| 10    | DMF:H <sub>2</sub> O                       | NaOH                            | 14       | 65                  |
| 11    | DMF:H <sub>2</sub> O                       | Na <sub>2</sub> CO <sub>3</sub> | 14       | 55                  |
| 12    | DMF:H <sub>2</sub> O                       | Et <sub>3</sub> N               | 14       | 90 <sup>c</sup>     |
| 13    | DMF:H <sub>2</sub> O                       | Et <sub>3</sub> N               | 14       | 95 <sup>d</sup>     |
| 14    | DMF:H <sub>2</sub> O                       | Et <sub>3</sub> N               | 14       | 88 <sup>e</sup>     |
| 15    | DMF:H <sub>2</sub> O                       | Et <sub>3</sub> N               | 14       | 95 <sup>f</sup>     |

**TABLE 2**Optimization of Cu sourcein water for Chan-Lam reaction

**TABLE 3**Optimization of reactioncondition for Chan-Lam reaction<sup>a</sup>

<sup>a</sup>Reaction Condition: aniline (0.5 mmol), phenyl boronic acid(1 mmol), base(2 equiv.), 10 mol% of Cu(OAc)<sub>2</sub> and Ligand L, RT, solvent (4 mL) in air.

<sup>c</sup>amount of base decreased to 1 equiv.

<sup>d</sup>Amount of base increased up to 3 equiv.

eAmount of catalyst decreased up to 5 mol%.

<sup>f</sup>Amount of catalyst increased up to 15 mol%.

square planar geometry around Cu(II) and could be assigned to ligand to metal charge transfer transition (Figure 5).<sup>[12]</sup>

### 2 | CATALYTIC APPLICATION

After synthesizing the 2, 5-dimethoxybenzaldehyde-4-pheny lthiosemicarbazide ligand and its precursor complex of Cu(II)

(as shown in Scheme 1) by using methods reported earlier, our next attempt is to investigate its catalytic efficiency in Chan-Lam cross-coupling reaction. We have performed a series of control experiments. No conversion was observed in the absence of any one of these reaction parameters (Table 1, entries 1-5). From the results, it was clear that the base, solvent, and Cu source are all essential for this reaction, indicating their key role in this transformation reactions.

<sup>&</sup>lt;sup>b</sup>Isolated yield.





TABLE 4 (Continued)



Next, we optimized the reaction conditions taking aniline and phenyl boronic acid as model substrate and using the synthesized ligand. The reactions were performed successfully at room temperature. To get the effective results of the Chan-Lam reaction, the reaction condition was first optimized by considering the effect of different Cu sources such as  $Cu(OAc)_2 \cdot H_2O$ ,  $CuSO_4 \cdot 5H_2O$ ,  $CuCl_2 \cdot 2H_2O$  (Table 2, entries 1-6) etc. From this study, it was observed that  $Cu(OAc)_2 \cdot H_2O$  catalyses very well with the ligand (Table 2, entry 4). However, it was observed that the pre-formed complex comparatively gave lower yield than the in situ complex (Table 2, entry 6).

On investigating the effect of different solvents such as <sup>*i*</sup>PrOH, water, acetonitrile, MeOH, and DMF showed that solvent with higher polarity index were more efficient (Table 3, entries 1-8). Among these a mixture of DMF:H<sub>2</sub>O in 1:1 proportion was found to be the best solvent (Table 3, entry 8).

As bases play significant role in the reaction of arylboronic acid by activating the boronic acid during the course of the reaction, we further investigated the effect of different inorganic and organic bases such as  $K_2CO_3$ ,  $Na_2CO_3$ , NaOH, and  $Et_3N$  for this reaction (Table 3, entries 8-11). Out of these,  $Et_3N$  was found to be the best base (Table 3, entry 8). Furthermore, 2 equiv. base gave maximum yield and on increasing its amount did not improve the product yield, whereas lowering its amount decreases the product yield (Table 3, entries 12 & 13).

Next, we decided to optimize the amounts of catalyst in the reaction using various amounts of the ligand and Cu salt. It was found that decreasing the amount of catalyst resulted in lower yields under the same conditions (Table 3, entry 14), whereas increasing its amount did not improve the yield or reaction time (Table 3, entry 15). Then, we fruitfully applied the optimized condition for the Chan-Lam crosscoupling reaction with different N-heterocycles and arylboronic acid (Table 4). Notably, aniline reacts with different arylboronic acid in short duration of time compared to imidazole derivatives. However, the substituents in the imidazole ring such as 2-ethyl imidazole and n-methyl imidazole gave lower yield compared to imidazole (Table 4, entries 10 & 11). Interstingly, our present protocol is also very efficient for benzimidazole, pyrazole, and 4-bromoindole (Table 4, entries 7-9). It was also noticed that arylboronic acid bearing both electron donating and electron withdrawing substituent group gave satisfactory yield (Table 4, entries 2-4 and 12,13). Also, heteroboronic acid (thioenyl boronic acid) gave good yield employing this protocol (Table 4, entries 5 & 14).

In summary, we have developed a new protocol for the Chan-Lam cross-coupling reaction between arylboronic acid and various N-heterocycles. The main advantageous features of our protocol include (i) use of water as cosolvent, (ii) the reaction proceeds well at room temperature,

## 8 of 10 WILEY Heteroatom

| N-based neucleophiles | Reaction condition   | Yield% | References   |
|-----------------------|--|--------|--------------|
| Aniline               | Cu(II) Schif base complex (8 mol%), K <sub>2</sub> CO <sub>3</sub> (2 equiv.), CH <sub>3</sub> CN, $\triangle$         | 66-85  | [6b]         |
| Imidazole             | -  | -      |              |
| Pyrazole              | -  | -      |              |
| Indole                | -  | -      |              |
| Aniline               | Cu complex (20 mol%), $K_2CO_3$ (3 equiv.), $H_2O$ , RT, air   | 71-95  | [6a]         |
| Imidazole             | Cu complex (5 mol%), K <sub>2</sub> CO <sub>3</sub> (2 equiv.), <i>i</i> -PrOH, RT, air                                | 63-94  |              |
| Pyrazole              | -  | -      |              |
| Indole                | -  | -      |              |
| Aniline               | Cu complex (40 mol%), Et <sub>3</sub> N (2 equiv.), DCM, RT, air   | 66     | [7]          |
| Imidazole             | -  | -      |              |
| Pyrazole              | -  | -      |              |
| Indole                | -  | -      |              |
| Aniline               | -  | -      | [6c]         |
| Imidazole             | Cu(II) complexes with Nitrogen-Chelating Bidentate Ligands (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , O <sub>2</sub> | 32-63  |              |
| Pyrazole              | -  | -      |              |
| Indole                | -  | -      |              |
| Aniline               | Cu complex (5 mol%), $Et_3N$ (2 equiv.), DMF:H <sub>2</sub> O, RT  | 74-95  | Present work |
| Imidazole             | Cu complex (5 mol%), Et <sub>3</sub> N (2 equiv.), DMF:H <sub>2</sub> O, RT  | 70-94  |              |
| Pyrazole              | Cu complex (5 mol%), Et <sub>3</sub> N (2 equiv.), DMF:H <sub>2</sub> O, RT  | 81     |              |
| Indole                | Cu complex (5 mol%), Et <sub>3</sub> N (2 equiv.), DMF:H <sub>2</sub> O, RT  | 78     |              |

TABLE 5 Comparison of present work with earlier reports

and (iii) the present protocol is very effective for formation of C-N bond between various arylboronic acids and N-heterocycles including pyrazole, 4-bromoindole etc. in aqueous media and at room temperature with good yield.

### 3 | EXPERIMENTAL

### 3.1 | Materials and methods

2,5-dimethoxybenzaldehyde and 4-phenylthiosemicarbazide were purchased from Spectrochem. The Cu salts such as  $Cu(OAc)_2 \cdot H_2O$ ,  $CuCl_2 \cdot 2H_2O$  were purchased from Rankem. The bases used in the reactions were received from Sigma-Aldrich. The substrates used were purchased from Sigma-Aldrich, Spectrochem, and Rankem. All other chemicals and solvents were purchased from different Indian firms.

The synthesized ligand L was characterized by FT-IR and ( ${}^{1}$ H &  ${}^{13}$ C) NMR spectral analysis. The FT-IR spectra of the ligand and complexes were recorded in a Shimadzu Prestige 21 FT-IR spectrophotometer using KBr disks in the range 4000-250 cm<sup>-1</sup>. The mass spectra were received from SAIF, Punjab University using Waters, Q; TOF Micromass (LC-MS) in DMSO-d<sub>6</sub> as solvent. The  ${}^{1}$ H (400.23 MHz) and  ${}^{13}$ C (100.64 MHz) NMR spectra were obtained from SAIF, IISc, Bangalore using DSX-300, AV-700 NMR spectrometer. As the prepared Cu complex is paramagnetic in nature, so

the <sup>13</sup>C and <sup>1</sup>H NMR spectra of the complex could not be resolved. Therefore, we have characterized the complex only by FT-IR, UV-Visible, and ESR study.

### 3.1.1 | Synthesis of 2,5-dimethoxybenzaldehyde-4-phenylthiosemicarbazide (L)

A mixture of 2,5-dimethoxybenzaldehyde(1.66 g, 10 mmol) and 4-phenylthiosemicarbazide(1.65 g, 10 mmol) in 25 mL ethanol with few drops of glacial acetic acid was refluxed at 65°C for 4 hour. After completion of the reaction (monitored by TLC), the resulting solution was cooled to room temperature, whereupon a white microcrystalline product was obtained. The solid product was filtered off, washed with ethanol, and was dried over fused  $CaCl_2$  in a desiccator. The crude product was purified by recrystallization from ethanol.

### 3.1.2 | Synthesis of Cu(II) complex (C)

A mixture of  $CuCl_2 \cdot 2H_2O$  (0.850 g, 5 mmol) and the ligand L (1.575 g, 5 mmol) in 50 mL acetonitrile was refluxed for 3 hour. A yellow colored precipitate was formed, which was filtered off, washed with acetonitrile, and dried over fused  $CaCl_2$  in a desiccator. The reactions involved in the formation of ligand L and complex C were shown in Scheme 1.

# **3.2** | General procedure for the Chan-Lam cross-coupling reaction

A mixture of 0.5 mmol of aniline, 0.75 mmol of arylboronic acid, 2 equiv. of base, ligand L, and  $Cu(OAc)_2 \cdot H_2O$  (in 1:1 molar ratio) in 4 mL of DMF:H<sub>2</sub>O as solvent was stirred at room temperature for appropriate time. The progress of the reaction was monitored by TLC. When the reaction was completed (monitored by TLC), the mixture was diluted with (3 × 20 mL) of water and extracted with ethylacetate (20 mL). Then the organic layer was washed with brine solution and dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solution was evaporated in a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel 60-120 mesh using hexane/ethyl acetate (9:1) to obtain the desired product. The purity of the compound was further confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-MS data.

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