



## Efficient N-arylation catalyzed by a copper(I) pyrazolyl-nicotinic acid system

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### ABSTRACT

Catalyst 6-(1*H*-pyrazol-1-yl)nicotinic acid L-CuCl behaves as a very active promoter of the N-arylation reactions, as it has been demonstrated with varieties of substrates under mild reaction conditions. A Cu(I) complex based on L of precatalyst has been isolated by a hydrothermal method and structurally characterized.

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### 1. Introduction

N-arylation is an important transformation in organic synthesis, and the products have high utilities in synthetic chemistry, life sciences, and polymer industries.<sup>1–3</sup> Catalysis in this type of reaction by low-cost and environmental-friendly copper is attracting considerable attention, due to the potential for the industrial and practical applications. During the last decade, some remarkable achievements in copper-catalyzed N-arylation reactions have been made.<sup>4–13</sup> Most of these cases are performed with CuI as the catalyst, and other Cu sources, such as inexpensive Cu<sub>2</sub>O and CuCl with low sensitivity to light and air are rather limitly used.<sup>14–18</sup> Ligand identification to promote efficient and economical N-arylation reactions is of stimulating interest in such catalytic system.<sup>19–21</sup> Much effort is still needed in the search for new ligands that can be used to further improve the efficiency and generality of copper-catalyzed N-arylation.<sup>22–26</sup> Indeed, *N*-heterocycles carboxylic acid ligands have been demonstrated as highly effective ancillary ligand for accelerating Cu(I)-catalyzed C–N bond-forming processes,<sup>27–30</sup> probably because they bond to the metal centers through the carboxylate group to make the Cu(I) species more reactive toward an eventual first oxidative addition or coordination of the substrate aryl halide.<sup>31</sup> Also, pyrazole and its derivatives are found previously to be quite effective for coupling of a variety of nitrogen-containing heterocycles with aryl halides.

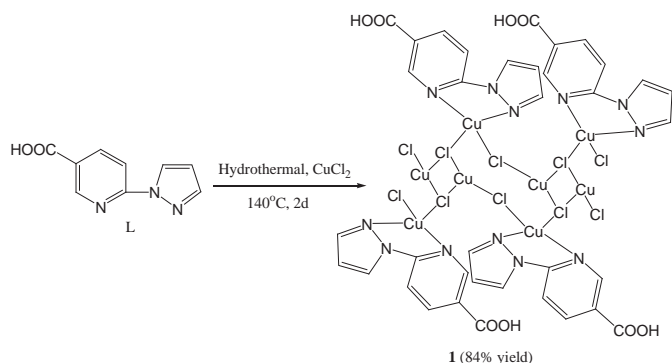
Consequently, we have selected a new combined ligand 6-(1*H*-pyrazol-1-yl)nicotinic acid (L), that is, an ideal bidentate chelator containing two coordinating nitrogen atoms generated from introducing a pyrazolyl group at the 1-position of the nicotinic acid, to unravel its catalytic activity for C–N bond-forming reaction. Additionally, the multidentate ligands display externally as simple added reagents, the copper/ligand catalytic processes have not been well-determined, especially the structures of Cu(I) precatalysts are rarely investigated.<sup>32–34</sup> In this paper, we describe the ligand 6-(1*H*-pyrazol-yl)nicotinic acid and its promising catalytic application with CuCl in arylation of *N*-nucleophiles. Concurrently a dark red Cu(I) complex Cu(L)Cl·CuCl (**1**) with a 1D double-chain structure as Cu(I)-precatalyst was synthesized with a good yield from the ligand (L) with copper chloride dihydrate under a special hydrothermal reduction condition.

### 2. Results and discussion

From the lower cost starting materials, ligand L was easily prepared through the substitution reaction at nitrogen of deprotonated pyrazole with methyl 6-chloronicotinate and acidic hydrolysis in high yield and on a multigram scale.<sup>35</sup> Treatment of the ligand L with CuCl in THF gave an organic precipitate. The resulting product is almost insoluble in common organic solvents except in DMF and it is thus difficult to determine structural information and satisfactory analytical data. Fortunately, hydrothermal reduction treatment of L and CuCl<sub>2</sub> was effective to generate the Cu(I) complex **1** based on ligand L by the reduction of CuCl<sub>2</sub> with 4-hydroproline as a reducing additive agent (Scheme 1).

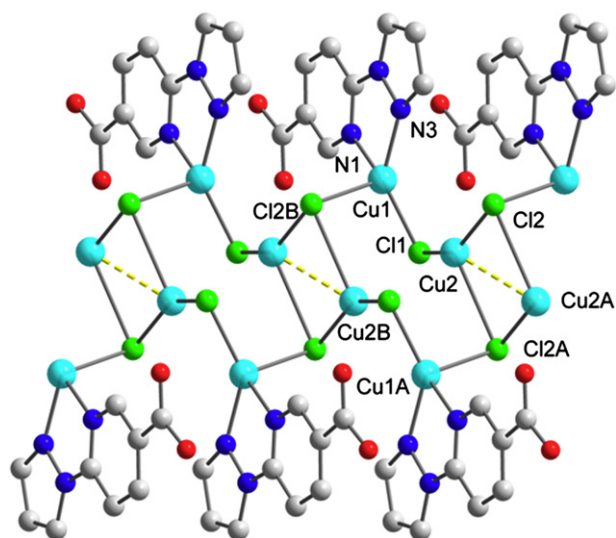
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When using CuCl as the starting reagent without the reductant, single-phase **1** could not be obtained. The successful incorporation of ligand L inside the structure of **1** was confirmed with elemental (C, H, N) analyses, and by comparison of the observed powder XRD patterns with that generated from single-crystal structural data.



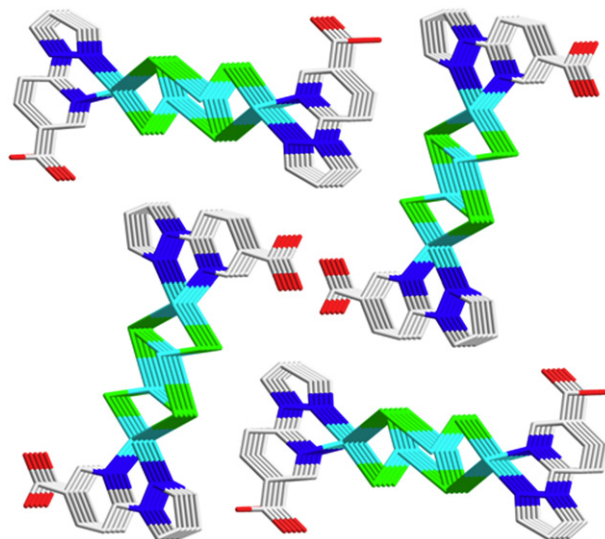
**Scheme 1.** Preparation of Cu(I) complex (**1**) from ligand 6-(1H-pyrazol-yl)nicotinic acid (L).

Complex **1** is stable in air or water for several months, and insoluble in water and common organic solvents, such as ethanol, acetone, acetonitrile, and THF but soluble in DMF. It crystallizes in a monoclinic system with space group  $P2_1/c$ . In the structure of **1**, there are two types of Cu coordination environments. The Cu(1) site is coordinated by two nitrogen donors of the rigid ligand fragment and by two Cl atoms to furnish a distorted tetrahedral geometry. The distance between Cu(1) and N(1) is 2.135(5) Å, whereas the distance between Cu(1) and N(3) is 2.000(5) Å. Cu(2) is trigonal-coordinated by one  $\mu_2$ -Cl atom and two  $\mu_3$ -Cl atoms (Fig. 1). The two different Cu atoms are joined together through the common  $\mu_2$ -Cl atom to form infinite 1D double-chain  $[Cu_2Cl_2L]_n$  along the  $c$  axis. It is interesting to stress that in **1** two Cu(1) atoms and two Cu(2) atoms bridged by two  $\mu_2$ -Cl atoms and two  $\mu_3$ -Cl atoms, form a distorted 8-ring  $[Cu_4Cl_4]$  and a cyclic  $[Cu_2Cl_2]$  core in which the four atoms are nearly located in a plane. The intermolecular Cu(2)⋯Cu(2A) distance of 2.852(17) Å in the complex is much longer than that in Cu metal, showing the existence of weakly bonding interactions between the  $d^{10}$  copper atoms.<sup>36–38</sup> The angles of Cu(1)–Cl(1)–Cu(2) and Cl(1)–Cu(2)–Cl(2A) are



**Fig. 1.** View of the complex **1** (color codes: Cu cyan, Cl green, O red, N blue, C gray).

87.69(6)° and 97.41(6)°, respectively. In the solid-state structure of **1**, the electron-withdrawing carboxylic acid groups of ligands are not coordinated to metal copper atom and extend outboard of the chains (Fig. 1). The chains in **1** are held together tightly mainly through electrostatic interactions resulting in its poor solubility except in DMF (Fig. 2). The result should provide good insight on solvent choice for improved catalytic applications of **1**.



**Fig. 2.** One-dimension chain structure of **1** along the  $a$ -axis (color codes: Cu cyan, Cl green, O red, N blue, C gray).

The catalytic activities of complex **1** and the designed ligand L together with copper(I) were initially evaluated by using the C–N coupling of bromopyridine with pyrazole as a model reaction. The N-arylation of nitrogen-containing heterocycles is of great interest due to the importance of the resulting products with possible synthetic applications in biochemistry and medical science. The accelerating effectivity of the ligand L toward N-arylation of pyrazole with bromide pyridine in DMF with different bases under a 10 mol % catalytic copper is given in Table 1. The preliminary studies revealed that the aryl bromide can be successfully coupled with pyrazole at 100 °C in the presence of catalytic amounts of CuCl and the ligand L (Cu/L=1:1) to afford a 99% yield of the desired product 2-(pyrazol-1-yl)pyridine. Noticeably, this work was carried out on a 5 mmol scale and demonstrated that this reaction has the potential for gram-quantity production. Both  $K_3PO_4$  and  $Cs_2CO_3$

**Table 1**  
Cu-catalyzed N-arylation of pyrazole<sup>a</sup>

Entry	Cu source	Ligand	Base	Yield <sup>b</sup> [%]
1	CuCl	—	$Cs_2CO_3$	<20
2	CuCl	L	$Cs_2CO_3$	92
3	<b>1</b>	—	$Cs_2CO_3$	87
4	CuCl	L	$K_3PO_4$	99
5	CuCl	L	$K_3PO_4 \cdot 3H_2O$	91
6	CuCl	L	$K_2CO_3$	85
7	$Cu(CH_3CN)_4PF_6$	L	$K_3PO_4$	81
8	$Cu_2O$	L	$K_3PO_4$	74

<sup>a</sup> Reaction conditions: copper compound (0.5 mmol), ligand 6-(1H-pyrazol-yl)nicotinic acid (L) (0.5 mmol) or **1** (0.5 mmol), pyrazole (7.5 mmol), 2-bromopyridine (5 mmol), base (10 mmol), DMF (20 mL).

<sup>b</sup> Isolated yield after silica-gel flash chromatography (average of two runs).

gave better results in DMF. When using  $K_3PO_4 \cdot 3H_2O$  as the base, the yield only decreased a little bit, indicating that this system was not very sensitive to trace water. The accelerating effect of L is evident when a similar ligand-free reaction by CuCl returned below 20% yield (Table 1, entry 1), and 2-bromopyridine is often known less reactive. More importantly, the catalyst was proved to be particularly efficient, as even a 5 mol % catalyst loading furnished the product in 72% yield. When the discrete complex **1** was used with  $Cs_2CO_3$  as a base, a conversion of 87% was achieved (entry 3), which is similar as when the copper(I) catalytic species were generated in situ from ligand L and CuCl (entry 2). The use of other copper sources, such as  $Cu(CH_3CN)_4PF_6$  (entry 7) and  $Cu_2O$  (entry 8) together with ligand L resulted also in satisfying isolated yields. The high activity contributes possibly to the rigid chelating spacer of L, which might provide better skeletal support to the metal copper.<sup>39,40</sup> It should be pointed out that, the exact nature of catalytically active species of **1** is not clear, because the chain structure of **1** might be broken in polar DMF and the formed activated Cu(I) species bearing one ligand L probably promote the reaction efficiency as well, which has been reported previously for similar catalytic behavior of the one-dimensional coordination polymer  $[Cu_2I_2L]_n$  (L=[NNNN] ligand).<sup>34</sup>

With the optimized procedure in hand, the CuCl/L catalytic system was applied to the selective arylation of imidazole and pyrazole with aryl bromides in DMF. As depicted in Table 2, in the presence of excess of  $K_3PO_4$  as the base at 100 °C, N-arylation products were afforded in good yields except that only small amount of the desired product was detected when 4-pyrazolecarboxylic acid was employed. The possible reason for low yield in the case of 4-pyrazolecarboxylic acid is the poor solubility

**Table 2**  
C–N Coupling products catalyzed by CuCl/L system in the N-arylation of imidazole and pyrazole<sup>a</sup>

Entry	Ar–X	Nucleophile	Product	Yield <sup>b</sup> [%]
1				85
2				91
3				94
4				81
5				96
6				76
7				88
8				84 <sup>c</sup>

<sup>a</sup> Reaction conditions: CuCl (0.5 mmol), ligand 6-(1*H*-pyrazol-1-yl)nicotinic acid (L) (0.5 mmol), N-nucleophiles (7.5 mmol), aryl halide (5 mmol),  $K_3PO_4$  (10 mmol), DMF (20 mL), reaction temperature 100 °C, reaction time 24 h.

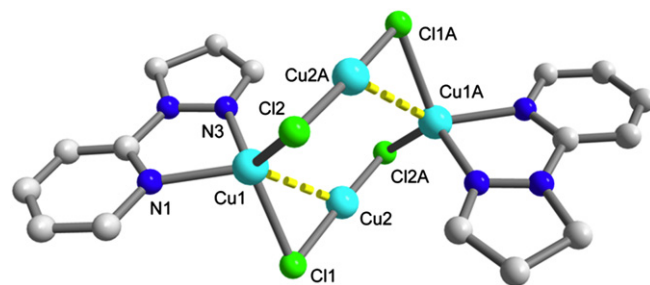
<sup>b</sup> Isolated yield [%] after silica-gel flash chromatography (average of two runs).

<sup>c</sup> 10 mmol of pyrazole was used.

of potassium salt produced from 4-pyrazolecarboxylic acid and  $K_3PO_4$  in DMF. The coupling of imidazole with bromobenzene afforded the corresponding *N*-phenylimidazole in a yield of 91%. And the arylation of imidazole with 2-bromopyridine gave a 94% yield. We also observed that the *N*-arylation of 1-chloro-4-iodobenzene with twofold excess of pyrazole afforded exclusively the mono *N*-arylpyrazole product in satisfactory yield. Such reactions include nitrogen-containing heterocycles were previously performed with CuI as the catalyst. Here, in combination with the lower cost CuCl, the ligand L exhibited very high catalytic activity for the *N*-arylation under mild reaction conditions.

The products of arylation reactions were multidentate nitrogen-containing compounds, which were also used as *N*-donor chelating reagents in coordination chemistry for transition-metal catalysis or medicinal chemistry.<sup>41,42</sup> The product 2-(pyrazol-1-yl)pyridine (L1) (in Table 1) turns out to be a complexing agent for Cu(I). Herein we synthesized a new tetranuclear Cu(I) complex  $Cu_4Cl_4(L1)_2$  (**2**) from L1 and  $CuCl_2$ . The dark red complex **2** was obtained with the similar condition for **1**. Complex **2** crystallizes in the triclinic, space group *P*–1.

The structure of **2** also contain two different Cu(I) atoms. Cu(1) is four-coordinated by two nitrogen atoms from bidentate ligand L1, and two  $\mu_2$ -Cl atoms, exhibiting a distorted tetrahedral geometry. Cu(2) is bidentated by Cl(1) and Cl(2) atoms. Notably, Cu(1) and Cu(2) are bridged by two  $\mu_2$ -Cl atoms, forming an distorted  $[Cu_4Cl_4]$  ring structure (Fig. 3). The angles of Cu(1)–Cl(1)–Cu(2) and Cu(1)–Cl(2)–Cu(2A) are 76.42(7)° and 81.25(7)°, respectively. Though the Cu1–Cu2 distances are confined to a short separation of 2.786 (14) Å, there is no Cu–Cu formal bonding expected. The structure of complex **2** is different from that of the complex **1**, and even unlike that of dinuclear Cu(I) coordination complex based on other pyridine ligands. The distance of Cu(1) and N(1) atom from pyridine group (2.115(6) Å) also has longer than that of Cu(1) and N(3) from pyrazole group (2.039(6) Å) (Fig. 3). Since the interesting structure of complex **2**, we expect its catalytic application for analogic reaction systems in our further study. The rationality of the structures of **1** and **2** is confirmed by valence bond theory. According to the Brown parameters,<sup>43</sup> the valence bond sum of each Cu(I) cation in the two complexes based on strength analysis is consistent with the expected formal oxidation states, suggesting that both two structures are reasonable.



**Fig. 3.** View of  $[Cu_4Cl_4]$  ring structure in **2**.

### 3. Conclusions

In conclusion, we have demonstrated that 6-(1*H*-pyrazol-1-yl)nicotinic acid L mixed with CuCl can efficiently promote *N*-arylation reactions of nitrogen-containing heterocycles with aryl bromides, and a simple and powerful Cu(I) complex **1** for single-molecular catalysis was determined by single crystal X-ray diffraction analysis. We anticipate that the successful synthesis of **1** may assist in the design and exploitation of stable new precatalysts with useful applications.

## 4. Experimental section

### 4.1. General methods

All the C–N bond-forming reactions were carried out under N<sub>2</sub> atmosphere by using standard Schlenk techniques. DMF was distilled under vacuum over CaH<sub>2</sub>. Unless otherwise indicated, all chemicals were used as received without purification. NMR spectra were recorded in CDCl<sub>3</sub> with chemical shifts referenced to SiMe<sub>4</sub> as internal standard on Bruker AMX500 500 MHz FT NMR spectrometers. The powder XRD patterns (Cu K $\alpha$  radiation) were recorded on a Rigaku RINT2000 diffractometer with a graphite monochromator at room temperature. Analyses for C, H, and N were carried out on a Perkin–Elmer 240C analyzer. Mass spectra were obtained on a Finnigan spectrometer in ESI mode. Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda=0.71073$  Å). The structures were solved by the direct method and refined by the full-matrix least-squares method on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms.

**Synthesis of complex 1:** A mixture of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.5 mmol, 0.085 g), **L** (0.25 mmol, 0.045 g), 4-hydroproline (0.25 mmol, 0.033 g), and H<sub>2</sub>O (10 mL) was heated at 140 °C in a Teflon-lined stainless steel autoclave for 2 days. Afterward, the reaction system was slowly cooled to room temperature, dark red block crystals were obtained in about 84% yield (0.081 g) based on Cu. Elemental analysis: C 28.21, H 2.03, N 10.74% (calcd: C 27.92, H 1.82, N 10.85%). Moreover, no changes in color or powder XRD pattern of the compound could be detected after keep in air for several months.

The synthetic procedure for **2** was identical to that for **1**, except that instead of ligand, **L1** (0.25 mmol, 0.045 g) was used as ligand. Dark red crystals were obtained in about 32% yield (0.027 g) based on Cu. This complex was also insoluble in water and common organic solvents. Elemental analysis: C 27.86, H 2.01, N 12.11% (calcd: C 28.01, H 2.05, N 12.25%).

Crystal data for **1** (C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>Cu<sub>2</sub>) (CCDC 772363),  $M=387.17$ , monoclinic, space group  $P2_1/c$ ,  $a=5.007(2)$ ,  $b=16.861(7)$ ,  $c=14.454(6)$  Å,  $\beta=102.50(13)^\circ$ ,  $V=1191.3(8)$  Å<sup>3</sup>,  $Z=4$ ,  $\rho=2.153$  g cm<sup>-3</sup>, 2342 reflections measured, of which 1835 were unique ( $R_{\text{int}}=0.0388$ ),  $R_1=0.0523$ ,  $wR_2=0.1156$  ( $I>2\sigma$ ), GOF=1.031.

Crystal data for **2** (C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>Cl<sub>4</sub>Cu<sub>4</sub>) (CCDC 772364),  $M=686.29$ , triclinic, space group  $P-1$ ,  $a=7.4675(13)$ ,  $b=9.1257(15)$ ,  $c=9.5426(16)$  Å,  $\beta=74.19(2)^\circ$ ,  $V=550.3(16)$  Å<sup>3</sup>,  $Z=1$ ,  $\rho=2.358$  g cm<sup>-3</sup>, 2117 reflections measured, of which 1309 were unique ( $R_{\text{int}}=0.0714$ ),  $R_1=0.0563$ ,  $wR_2=0.1004$  ( $I>2\sigma$ ), GOF=1.091.

### 4.2. General procedure for the copper-catalyzed N-arylation of nucleophiles

A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with a copper compound (0.5 mmol), ligand **L** (0.5 mmol) or **1** (0.5 mmol; without additional ligand), base (10 mmol), DMF (ca. 20 mL), imidazole or pyrazole (7.5 mmol), and aryl halide (5 mmol). After two additional cycles of evacuation/backfill with N<sub>2</sub>, the flask was sealed under N<sub>2</sub> atmosphere and stirred at 100 °C. The reaction duration was not vigorously optimized but generally carried out for 24 h for convenience. After the resulting mixture was cooled to room temperature, the precipitate was removed by filtration. After evaporation, the obtained residue was purified by flash silica-gel column chromatography to give the N-arylated product. Yields reported in this paper are of isolated material and represent an average of two independent runs. Compounds were characterized by the comparison of their <sup>1</sup>H and <sup>13</sup>C NMR with

those previously reported data. See Supplementary data for detailed characterization data.

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### Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.102. These data include MOL files and InChIKeys of the most important compounds described in this article.

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