



Chan–Lam cross-coupling reactions promoted by anionic copper(I)/iodide species with cationic methyl-((pyridinyl)-pyrazolyl)pyridin-1-ium



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ABSTRACT

Four anionic ligands including 1-methyl-3(or 4)-(1-(pyridin-2-yl)-1*H*-pyrazol-3-yl)pyridin-1-ium iodide ([3,2'-pypzpy]I, [4,2'-pypzpy]I) and 1-methyl-3(or 4)-(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)pyridin-1-ium iodide ([2,3'-pypzpy]I, [2,4'-pypzpy]I) are prepared. Reaction of CuI with [3,2'-pypzpy]I affords a mononuclear complex [CuI₂(3,2'-pypzpy)] (**1**) and a one-dimensional coordination polymer [(Cu₄I₆)(3,2'-pypzpy)₂]_n (**2**). Analogous reactions of CuI with [4,2'-pypzpy]I, [2,3'-pypzpy]I or [2,4'-pypzpy]I yield [Cu₄I₆(4,2'-pypzpy)₂] (**3**), [CuI₂(2,3'-pypzpy)] (**4**) and [CuI₂(2,4'-pypzpy)] (**5**), respectively. Relative to that of CuI, complexes **1–5** exhibit enhanced catalytic activities towards the Chan–Lam cross-coupling reactions of imidazole and arylboronic acids in a H₂O–MeCN (v/v=2:1). This catalytic system is involved in the C–N cross-coupling reaction and works for a variety of imidazole derivatives as well as arylboronic acids with different electronic properties.

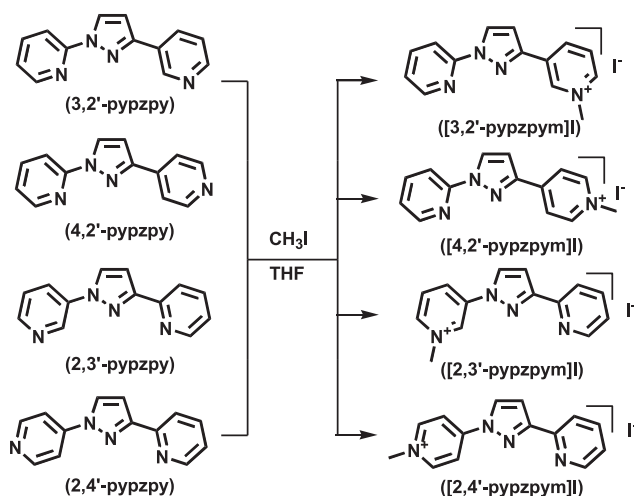
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1. Introduction

N-Aryl heterocycles have attracted increasing attention due to their wide applicability in biochemical, biological, medicinal and material sciences.¹ The most straightforward routes for synthesis of *N*-arylazole derivatives involve copper-mediated Ullmann-type coupling² and Pd-catalyzed Buchwald–Hartwig reaction of nitrogen-containing heterocycles with aryl halides.³ These reactions require expensive catalysts, or hard reaction conditions (such as high reaction temperature) and produce large amount of harmful wastes. Since 1998, the Chan–Lam coupling reaction⁴ has emerged as a highly efficient and valuable alternative to traditional methods for the construction of C–N bond due to the wide variety of commercially available boronic acids and the mildness of the reaction conditions.⁵ These reactions are often carried out in organic solvents⁶ or ionic liquids.⁷ It would be a greener and more economic approach if the Chan–Lam coupling reaction could be conducted in water or aqueous solvents. Recently, a number of

green water-soluble catalysts have been used to promote C–C cross-coupling reactions in water.⁸ So far, the homogeneous copper-catalyzed Chan–Lam cross-coupling systems in water or in aqueous solvents have less explored.⁹ Collman et al. reported that [Cu(OH)·TMEDA]₂Cl₂ could catalyze coupling reactions of imidazole with arylboronic acids in water with relatively low yields (up to 63%). It is noted that water-soluble catalysts could be obtained by incorporating hydrophilic moieties such as sulfonate, carboxylate, imidazolium salts, ammonium groups into the hydrophobic organic ligands. As our continuous effort on the syntheses of water-soluble metal coordination complexes¹⁰ and the formation of C–N bond,¹¹ we have designed and prepared a set of *N,N*-bidentate coordination ligands attached 1-methyl-pyridinium group (1-methyl-((pyridinyl)pyrazolyl)pyridin-1-ium iodide ([pypzpy]I)) (Scheme 1). Reactions of CuI with these ligands afforded five anionic [Cu_xI_y]-based coordination complexes [CuI₂(3,2'-pypzpy)] (**1**), [(Cu₄I₆)(3,2'-pypzpy)₂]_n (**2**), [Cu₄I₆(4,2'-pypzpy)₂] (**3**), [CuI₂(2,3'-pypzpy)] (**4**) and [(CuI₂)(2,4'-pypzpy)] (**5**). Compared with that of CuI, complexes **1–5** displayed greatly enhanced catalytic activities toward the coupling of imidazole with arylboronic acid in H₂O/MeCN (v/v=2:1). Described below are their syntheses, crystal structures and catalytic properties.

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Scheme 1. Synthesis of [pypzpy]I ligands.

2. Results and discussion

According to the literature,¹² reactions of 3-/4-(1*H*-pyrazol-3-yl)-pyridine with 2-iodopyridine or 2-(1*H*-pyrazol-3-yl)pyridine with 3-iodopyridine or 4-iodopyridine produced 2-(3-(pyridin-3-yl)-1*H*-pyrazol-1-yl)pyridine (3,2'-pypzpy), 2-(3-(pyridin-4-yl)-1*H*-pyrazol-1-yl)pyridine (4,2'-pypzpy), 2-(1-(pyridin-3-yl)-1*H*-pyrazol-3-yl)pyridine (2,3'-pypzpy) and 2-(1-(pyridin-4-yl)-1*H*-pyrazol-3-yl)pyridine (2,4'-pypzpy), respectively. As shown Scheme 1, reactions of 3,2'-pypzpy, 4,2'-pypzpy, 2,3'-pypzpy or 2,4'-pypzpy with excess MeI in refluxing THF for 12 h produced 1-methyl-3(or 4)-(1-(pyridin-2-yl)-1*H*-pyrazol-3-yl)pyridin-1-ium iodide ([3,2'-pypzpy]I, [4,2'-pypzpy]I) and 1-methyl-3(or 4)-(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)pyridin-1-ium iodide ([2,3'-pypzpy]I, [2,4'-pypzpy]I) in high yields. These four organic ligands were fully characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy, and mass spectrometry. Their high-resolution positive-ion mass spectra reveal that there exists one peak at $m/z=237.1142$ ([3,2'-pypzpy]I, [4,2'-pypzpy]I), 237.1140 ([2,3'-pypzpy]I) and 237.1146 ([2,4'-pypzpy]I), which can be assigned to the corresponding [pypzpy]⁺ cation. These cationic ligands are stable toward air and moisture, and freely soluble in H₂O, MeOH, DMSO, slightly soluble in CH₂Cl₂ and CHCl₃, but insoluble in toluene and Et₂O.

Diffusion of Et₂O into the MeCN solution containing CuI and [3,2'-pypzpy]I afforded red crystals of mononuclear complex [Cu₂(3,2'-pypzpy)] (1) and yellow crystals of 1D polymer [(Cu₄I₆)(3,2'-pypzpy)₂]_n (2) in 23% and 35% yields, respectively. The similar reaction in refluxing MeCN only produced 1 in a higher yield (88%). Refluxing of the MeCN solution of 2 could also produce complex 1. Reactions of CuI with [4,2'-pypzpy]I, or [2,3'-pypzpy]I or [2,4'-pypzpy]I in MeCN at room temperature resulted in the formation of one tetranuclear Cu(I) cluster [Cu₄I₆(4,2'-pypzpy)₂] (3) and two mononuclear complexes [Cu₂(2,3'-pypzpy)] (4) and [(Cu₂)(2,4'-pypzpy)] (5), respectively. Compounds 1–5 are also relatively air and moisture-stable. They are soluble in common organic solvents such as CH₂Cl₂, MeOH, EtOH and MeCN, DMF, DMSO and H₂O, but insoluble in Et₂O and *n*-hexane. The elemental analyses are consistent with their chemical formula. Their identities of 1–4 are finally confirmed by single-crystal X-ray crystallography. Numerous attempts to grow crystals of 5 always failed. As described below in this article, the sites of pyridinium group in pypzpy ligands have a significant influence on the anionic [Cu_xX_y]^{(y-x)-} structural motifs such as monomeric unit [Cu₂]⁻ in 1 and 4, chair-like unit [Cu₄I₆]²⁻ in 3 and ribbon chain

[Cu₄I₆]²ⁿ⁻ in 2. For the pypzpy ligands in 1–4, the cationic part on one end of its backbone is used to balance the anionic charges for anionic [Cu₂]⁻, [Cu₄I₆]²⁻ and [Cu₄I₆]²ⁿ⁻ aggregates. On the other end, the pyridyl and pyrazolyl groups in 1, 3 and 4 work together to chelate one Cu center in a *N,N'*-bidentate coordination fashion.

Being crystallized in the monoclinic space group *P*2₁/*n*, the asymmetric unit of 1 or 4 contains the discrete molecule [Cu₂(3,2'-pypzpy)] or [Cu₂(2,3'-pypzpy)]. Their cell parameters are essentially identical, and so are their molecular structures (Fig. 1 and Fig. S1). Therefore only the molecular structure of 1 is described below. Each Cu(I) in 1 is tetrahedrally coordinated by two I and two N atoms from 3,2'-pypzpy ligand. Compound 2 crystallizes in the triclinic space group *P*₁, and its asymmetric unit contains [Cu₂I₃]⁻ anion and one 3,2'-pypzpy cation. As shown in Fig. 2, I(1) atom bridges four Cu(I) atoms. The two adjacent Cu(I) atoms are further connected by μ-I⁻ ion, forming a pyramid-shaped structure. Such [Cu₄I₅] unit shares two [Cu₂I₂]⁻ rhomboids with two adjacent ones to form an infinite 1D anionic ribbon [Cu₄(μ₄-I)₂(μ-I)₄]²ⁿ⁻ running parallel to the *a* axis. Compound 3 crystallizes in the triclinic space group *P*₁, and its asymmetric unit has half a discrete molecule [Cu₄I₆(4,2'-pypzpy)₂]. It may be viewed as having a chairlike [(Cu(Cu))(μ-I)(μ₃-I)₂] core structure (Fig. 3). All Cu(I) centers in 3 are tetrahedrally coordinated by one μ-I, one μ₃-I and two N atoms of 4,2'-pypzpy and (Cu1 or Cu1A), or by one I, one μ-I and two μ₃-I atoms (Cu2 or Cu2A).

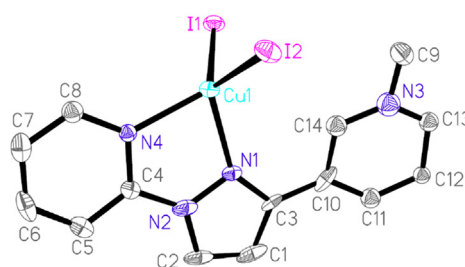
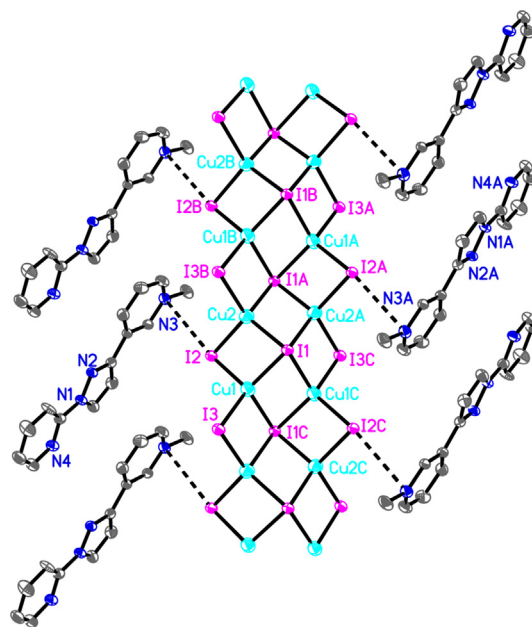


Fig. 1. View of the molecular structure of 1 with a labeling scheme and 50% thermal ellipsoids. All H atoms are omitted for clarity.

Fig. 2. View of the 1D [Cu₄(μ₄-I)₂(μ-I)₄]²ⁿ⁻ chain in 2 with a labeling scheme and 50% thermal ellipsoids. All H atoms are omitted for clarity.

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