

REGULAR ARTICLE

Silver(I) and copper(II)-imidazolium carboxylates: Efficient catalysts in Ullmann coupling reactions

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Abstract. The silver(I) and copper(II)-imidazolium carboxylate coordination assemblies were derived from the reaction between corresponding carboxylic acid ligands and metal salts. These new metal derivatives depict a novel structural motif with variable chemical and thermal properties. These metal complexes act as potential catalysts in Ullmann coupling reactions. The imidazolium linker present in these complexes plays a role as both ligand and counter ion to balance the metal charge.

Keywords. Copper(II); Silver(I); Coordination polymer; Imidazolium ion; Ullmann coupling.

1. Introduction

Carboxylate-functionalized imidazolium organic spacers are known as the most promising chelating ligands in proton conduction,¹ gas storage,^{2,3} and catalysis^{2,4-8} applications. For example, the well defined heterogeneous catalysts were derived from pre- or post-modified metal imidazolium derivatives.^{2,4-8} However, the synthetic approach for pre- or post-modified metal imidazolium derivatives are most challenging and very few examples have been demonstrated (Chart 1).

The first catalytic application of copper-palladium-imidazolium carboxylate for Suzuki–Miyaura cross-coupling reaction was demonstrated through post-modified route.⁴ Later, zinc-palladium-imidazolium carboxylate was reported through post-modified route for Suzuki–Miyaura coupling reaction, Heck coupling reaction, hydrogenation of olefins and reduction of nitrobenzene.⁴ The post-modified cobalt-imidazolium carboxylate-mediated synthesis of methyl ether from α , β -unsaturated ketone was reported.⁷ The first pre-modified zinc-copper-imidazolium carboxylate was reported for hydroboration of carbondioxide.⁶ Recently, we demonstrated the highly active lead(II)-imidazolium coordination assemblies for benzoin condensation reactions.⁸ In this paper, we report the first example of Ullmann reactions

mediated by silver(I) and copper(II)-imidazolium coordination polymers. These newly prepared catalysts are highly active towards Ullmann reaction.

2. Experimental

2.1 Materials and methods

The solvents were purchased from commercial sources and purified according to the standard procedures and freshly distilled under argon atmosphere prior to use.⁹ Unless otherwise stated, all the chemicals were purchased from commercial sources. 2-(1-(carboxymethyl)-1*H*-imidazol-3-ium-3-yl)acetate (**L¹H**) and 2-(1-(1-carboxyethyl)-1*H*-imidazol-3-ium-3-yl)propanoate (**L²H**) were prepared as previously reported.¹⁰ FTIR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV-Vis spectra were measured on a T90+ UV-Visible spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TASDT Q600, Tzero-press. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25°C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The crystal structures of **1** and **2** were measured on an Oxford Xcalibur 2 diffractometer. Single crystals of complexes suitable for the single crystal X-ray analysis were obtained from their reaction mixture at room temperature and the suitable single crystals for X-ray structural analysis were mounted at 150 K for **1** and 298 K for **2** in inert oil. Using Olex2,¹¹ the structure was solved with

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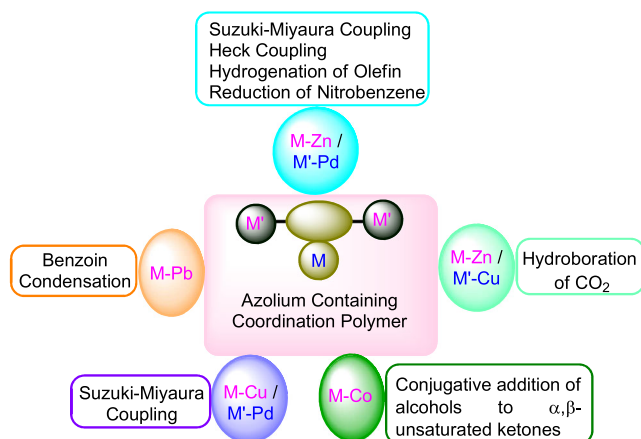


Chart 1. Known catalytic reactions with azolium-containing coordination polymers.

the ShelXS structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization. Absorption corrections were performed on the basis of multi-scans. Data quality of **2** was not very good. Molecule **2** depicted “B” level alerts. Attempts to get better quality data were not successful. This may be due to the copper X-ray source as well as the chiral centre present in the ligands as reported for similar work.^{10c} Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. ¹H NMR, ¹³C NMR and FT-IR data for **1** and **2** are shown in Figures S1–S6 (in Supplementary Information).

2.2 Synthesis of **1**

To a mixture of AgNO₃ (0.543 mmol, 0.092 g) and **L**¹**H** (0.271 mmol, 0.050 g), methanol (2 mL) and water (1 mL) was added, under stirring condition, until the reaction mixture became clear. The reaction mixture was maintained at room temperature for two days. Colourless crystals of **1** were obtained within 12 h. Yield: 52% (Based on AgNO₃). M.p.: 212–214°C (decomposed to black solid). FT-IR (Neat, $\bar{\nu}$ / cm⁻¹): 3341(b), 3113(m), 3071(m), 2999(m), 2960(m), 2326(w), 1734(m), 1567(s), 1329(s), 1289(vs), 1169(s), 1031(m), 965(m), 908(w), 862(m), 776(m), 691(s), 629(w), 576(w). ¹H NMR (DMSO-*d*₆, 400.13 MHz): δ 9.08 (s, 1H, ImH), 7.68 (d, 2H, ImH), 5.06 (s, 4H, CH₂) ppm. ¹³C NMR (DMSO-*d*₆, 100.613 MHz): δ 168.16 (C=O), 137.92 (ImC), 123.21 (ImC), 50.32 (CH₂) ppm.

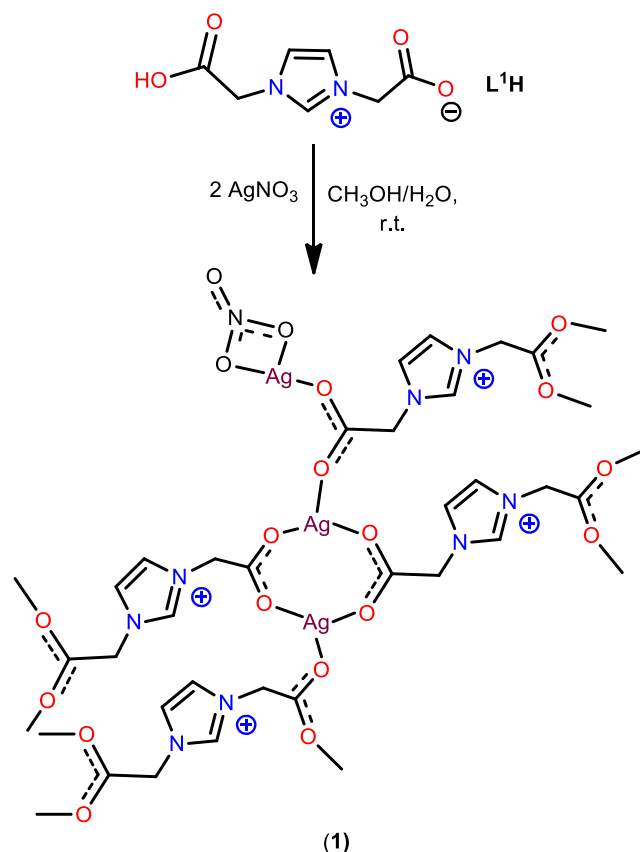
2.3 Synthesis of **2**

To a mixture of Cu(NO₃)₂·6H₂O (0.471 mmol, 0.113 g), **L**²**H** (0.235 mmol, 0.050 g) and HCOOH (0.235 mmol, 0.011 g), DMF (2 mL) and water (1 mL) was added; then, the suspension was heated at 80°C. The reaction mixture became

clear pale blue solution after 30 min and then the reaction condition was maintained at the same temperature for 12 h. The reaction mixture was slowly brought to room temperature to yield single crystals of **2** within 24 h. Yield: 48% (Based on Cu(NO₃)₂·6H₂O). M.p.: 218–220°C. FT-IR (Neat, $\bar{\nu}$ / cm⁻¹): 3419(b), 3149(m), 3081(m), 2933(m), 1663(vs), 1575(m), 1498(w), 1464(w), 1384(s), 1255(m), 1182(m), 1085(vs), 882(m), 791(w), 761(w), 737(w), 709(w), 661(s), 619(m). ¹H NMR (D₂O, 400.13 MHz): δ 8.32 (bs, 1H, ImH), 7.30 (bs, 2H, ImH), 2.92 (bs, 1H, CH), 2.76 (b, 2H, CH), 2.19 (bs, 3H, CH₃) ppm. ¹³C NMR (D₂O, 100.613 MHz): δ 165.67 (C=O), 137.12 (ImC), 121.95 (ImC), 37.08, 34.48, 31.50 (CH), 16.06 (CH₃) ppm.

2.4 Ullmann reaction

Oven-dried Schlenk was charged with catalyst (1 mol%) and iodobenzene and dried under vacuum for 5 min. Solvent (5 mL) was added under inert condition to the reaction mixture, evacuated for few seconds, refilled with nitrogen and then KOH (5 mol%) was added to the reaction mixture under nitrogen condition at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was diluted with water (10 mL) and DCM (10 mL). The organic phase was separated, washed with brine solution (7 mL), dried over anhydrous sodium sulphate and then the reaction mass was concentrated under reduced pressure to get



Scheme 1. Synthesis of **1**.

the crude compound. The crude compound was adsorbed on silica gel (100–200 mesh) for purification; then, petroleum ether and 10% ethyl acetate/petroleum ether (200 mL) were poured on the column to separate the final product.

3. Results and Discussion

The zwitterionic salt of **1** was isolated from the reaction between 2-(1-(carboxymethyl)-1*H*-imidazol-3-ium-3-yl)acetate (**L¹H**) and AgNO₃ (Scheme 1). The FT-IR spectrum of **1** showed the characteristic frequency at 1734 and 1567 cm^{−1} for the presence of mono and bidentate mode of carboxylate groups. The bidentate mode of coordinating NO₃[−] ion appears at 1329 and 1289 cm^{−1}. In ¹H NMR, the N–CH–N proton appeared at δ 9.08 ppm. The ¹³C NMR chemical shift value of C–O and N–CH–N carbons were detected at δ 168.1 and 137.9 ppm, respectively.

The solid state structure of **1** was further confirmed by single crystal X-ray diffraction technique (Figure 1). **1** crystallized in the monoclinic space group, C2/c

(Table 1). **1** is a first example of zwitterionic, two dimensional silver imidazolium carboxylate coordination polymer constructed by trinuclear silver (Figure 1).^{10b,c]} **1** consists of two different types of silver coordinated centres (Figure 1 (I and II)). Ag(1) and Ag(2) are tetracoordinated. The geometry and coordination environment of Ag(1) and Ag(2) centres in **1** are not comparable. The Ag(1)–Ag(1) bond distance is 2.804(8) Å. The geometry of Ag(1) can be described as distorted square planar and the coordination environment of Ag(1) is fulfilled by four carboxylate oxygen atoms (Figure 1 (I) and (II)). The square planar silver geometry is considered to be one of the rare coordination geometry for silver(I). Ag(2) is in distorted tetrahedral geometry by two monodentately coordinated carboxylate oxygen atoms and one nitrate ion. Notably, the trinuclear silver carboxylate coordination polymer with different geometrical arrangement is very rare.¹² The Ag(1)–O(4) bond distance (2.176(3) Å) is much shorter than that of Ag(2)–O(5) (2.540(4) Å). The O–Ag–O angle varies from 49.93(17)° (O(5)–Ag(2)–O(5)) to 160.47(12)° (O(3)–Ag(1)–O(4)).

The cationic salt **2** was obtained from the reaction between 2-(1-(1-carboxyethyl)-1*H*-imidazol-3-ium-3-yl)propanoate (**L²H**) and Cu(NO₃)₂·6H₂O (Scheme 2). The FT-IR spectrum of **2** shows the characteristic frequency at 1663 and 1575 cm^{−1} for the presence of bridging bidentate mode of coordinated carboxylate

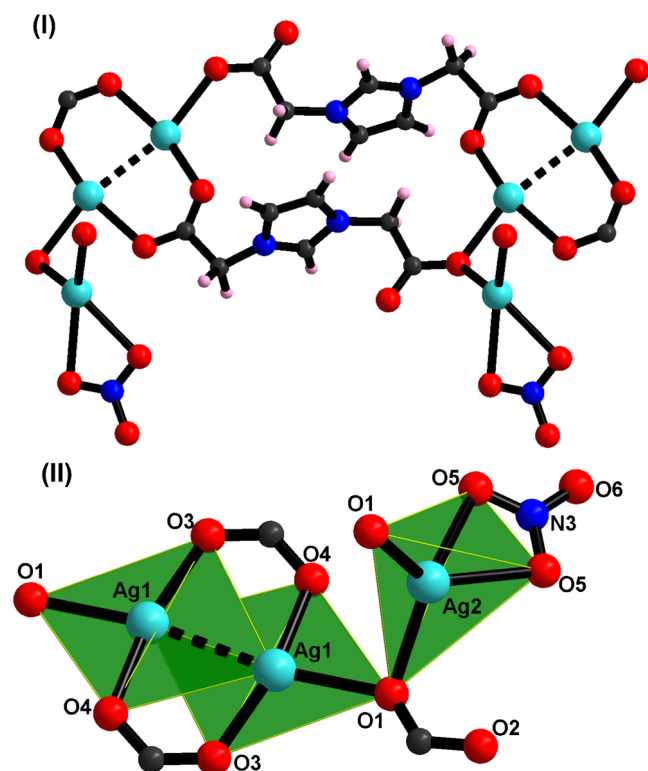
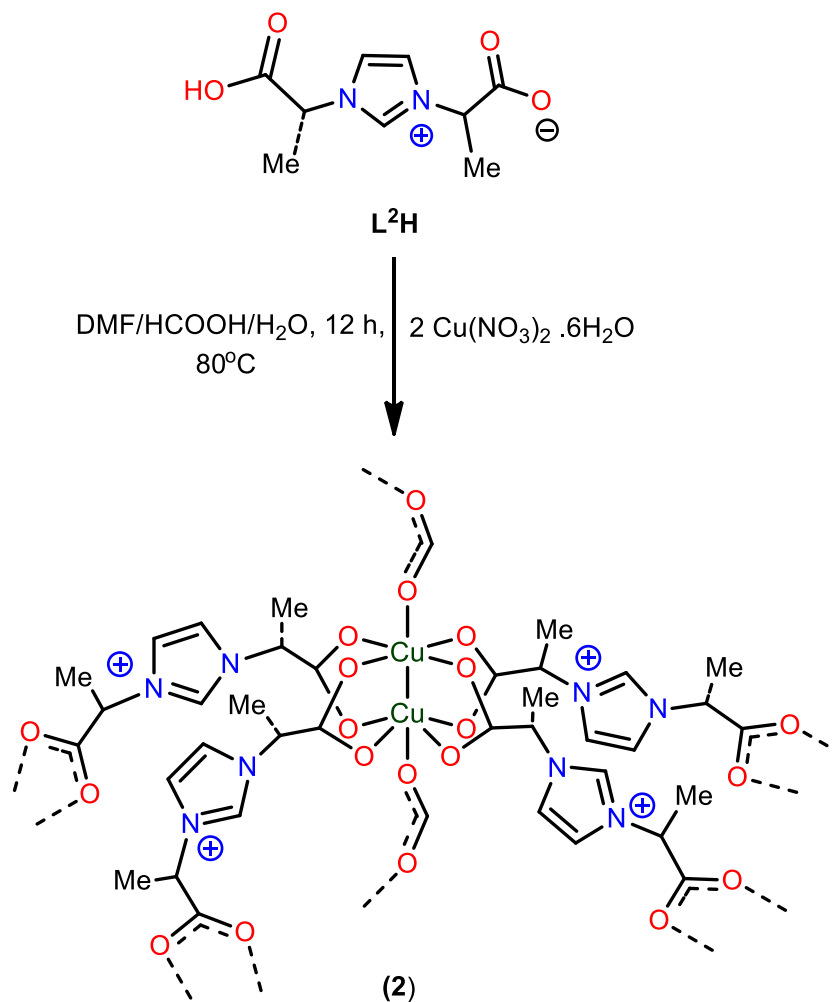


Figure 1. (I) The solid state structure of **1**. Selected bond lengths (Å) and angles (°): Ag(1)–O(1) 2.370(3), Ag(1)–O(4) 2.176(3), Ag(1)–O(3) 2.212(3), Ag(2)–O(1) 2.358(3), Ag(2)–O(5) 2.540(4), Ag(1)–Ag(1) 2.804(8), O(3)–Ag(1)–O(4) 160.47(12), O(1)–Ag(2)–O(1) 111.39(15), O(1)–Ag(2)–O(5) 107.67(12) & 135.92(13), O(5)–Ag(2)–O(5) 49.93(17); (II) Polyhedron arrangements of silver centre in **1**, Hydrogen atoms have been omitted for clarity.

Table 1. Structural parameters of **1** and **2**.

Parameters	1	2
Empirical formula	C ₁₄ H ₁₄ Ag ₃ N ₅ O ₁₁	C ₁₉ H ₂₂ Cu ₂ N ₄ O ₁₀
Formula weight	751.91	593.48
Temperature	150	293
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pnma
a/Å	21.6587(16)	16.0227(6)
b/Å	8.3304(3)	12.2031(5)
c/Å	13.6168(9)	21.2908(7)
α/°	90.00	90
β/°	127.000(11)	90
γ/°	90.00	90
Volume/Å ³	1962.1(2)	4162.9(3)
Z	4	4
ρ _{calc} /g/cm ³	2.545	0.947
Absorption coefficient/mm ^{−1}	3.039	1.575
F(000)	1448.0	1208.0
Reflections collected	4871	11196
Independent reflections	2261	3939
R _{int}	0.0335	0.0424
GOF on F ²	1.044	1.287
R ₁ values (all data)	0.0540	0.1195
wR ₁ values (all data)	0.0817	0.3256

Scheme 2. Synthesis of **2**.

group. In ^1H NMR, the N–CH–N proton appears at δ 8.32 ppm. In ^{13}C NMR, the chemical shift values for C–O and N–CH–N carbons are assigned at δ 165.6 and 137.1 ppm, respectively.

The solid state structure of **2** was further confirmed by single crystal X-ray diffraction technique (Figure 2). **2** crystallized in the orthorhombic space group, P_{nma} (Table 1). **2** is a one dimensional cationic coordination polymer. The one dimensional cationic coordination polymer of **2** is constructed by copper dimer, which are further bridged by one formate ion and two L^2 ligands. The copper dimer is in paddle wheel structure. The charge of each copper(II) dimer is balanced by one formate ion and two L^2 ligands. The geometry of copper is satisfied by five carboxylate oxygen atoms, one copper to copper short contact. As shown in Figure 2(II) carboxylates are bidentately bridged between two copper centres. The fifth coordination site is fulfilled by carboxylate moiety in monodentate fashion. The Cu–Cu bond distance is Cu(1)–Cu(2) (2.665(14) Å), which is considerably

longer than that of $[(\text{ddp})\text{GaCu}(\text{OTf})_2]$ (ddp = 2-diisopropylphenylamino-4-diisopropylphenylimino-2-pentene) (2.277(3) Å).¹³ The Cu–O bond distances are in the range from 1.965(4) Å (Cu(2)–O(7)) to 2.135(5) Å (Cu(1)–O(6)). The geometry and coordination types of copper centres are comparable. The O–Cu–O angles varies from 86.5(3)° (O(1)–Cu(1)–O(1)) to 167.70(16)° (O(3)–Cu(2)–O(2)).

The solid state and solution state UV-Vis absorption spectra of **1** and **2** are depicted in Figure S7 (Supplementary Information). The solid state UV-Vis absorption spectra of **1** and **2** are significantly different from those of solution spectra. In solution, the intense bands in **1** (263 nm) and **2** (270 nm) can be assigned to the $\pi \rightarrow \pi^*$ transition, while the absorption band at 427 nm can be attributed to the $n \rightarrow \pi^*$. In solid state, **1** gave a broad band, while **2** gave nearly three broad bands at 247 nm ($\pi \rightarrow \pi^*$), 373 nm ($n \rightarrow \pi^*$), and 767 nm (LMCT).

The thermal stability of **1** and **2** was analysed by TGA. Figure S8 (in Supplementary Information)

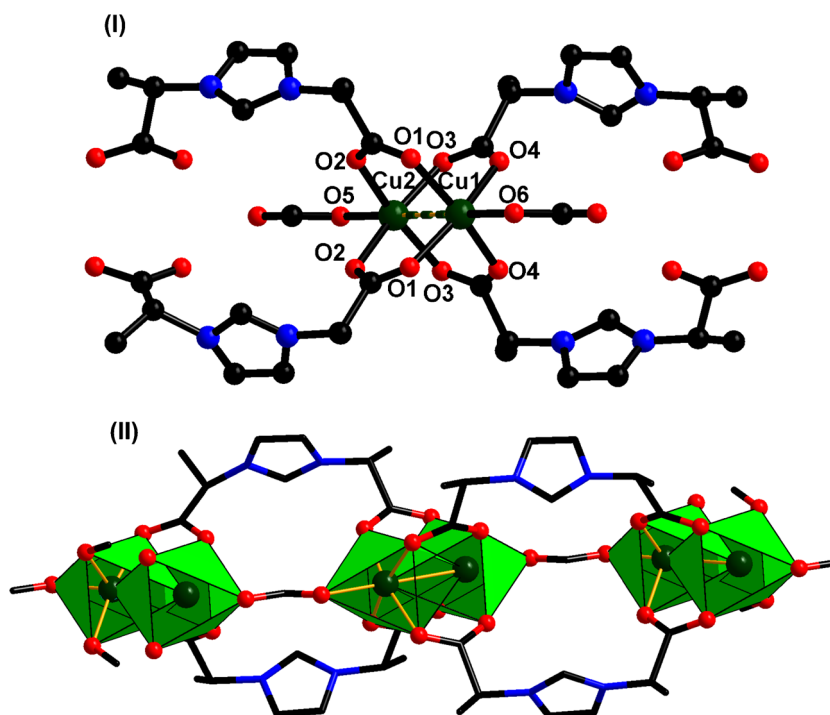


Figure 2. (I) The core structure of **2**. Hydrogen atoms in **2** have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1), 1.994(4), Cu(1)–O(4), 1.965(4), Cu(1)–O(6), 2.135(4), Cu(2)–O(2), 1.974(3), Cu(2)–O(3), 1.969(4), Cu(2)–O(5), 2.123(5), O(4)–Cu(1)–O(1), 167.63(16), O(3)–Cu(2)–O(2), 167.70(16); (II) The polyhedron arrangements of copper centre in **2**. Hydrogen atoms in **2** have been omitted for clarity.

reveals the thermal breakdown pathway of **1** and **2** based on thermal investigation under a flowing nitrogen atmosphere ($10^{\circ}\text{C min}^{-1}$, $30\text{--}1000^{\circ}\text{C}$). A small weight loss ($\sim 2\text{--}8\%$) was observed for **1** and **2** in the initial stage ($<80^{\circ}\text{C}$), which can be attributed to the loss of moisture. Complexes **1** and **2** showed the gradual weight loss from 200 to 500°C , which can be validated as the decomposition of organic moieties. Complex **1** shows gradual weight loss till 631°C , then remains unchanged till 1000°C . Similarly, complex **2** loses the major weight till 529°C and then remains unchanged till 1000°C .

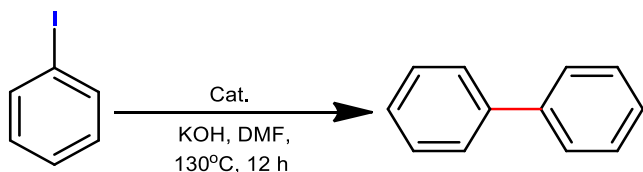
Furthermore, we attempted to use one mol% of coordination polymers **1** and **2** as catalysts for Ullmann reaction in DMF (Scheme 3). The catalytic reactions were analysed with iodobenzene at 130°C in the presence of five mol% potassium hydroxide as base in **1** and

2 (Table 2). In contrast to the known methodology,^{14,15} in this work, we used potassium hydroxide salt as deprotonation base to activate silver(I) and copper(II) imidazolium coordination polymers. The catalytic reaction was absent, when the reaction was carried out without catalyst (Table 2, entry 1). Poor Ullmann conversion was obtained when the reaction was carried out using only silver(I) and copper(II) salts (Table 2, entries 2–6). Similarly, the conversion was absent when the

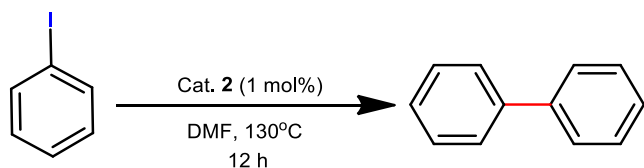
Table 2. Effect of catalyst on the Ullmann reaction.

Entry	Catalyst (1 mol%)	Isolated Yield (%) ^[a]
1	No	0
2	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	25
3	AgNO_3	10
4	CuCl_2	28
5	CuBr_2	31
6	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	25
7	L¹H	0
8	L²H	0
9	L¹H / AgNO_3	18
10	L²H / $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	37
11	1	58
12	2	85

[a] Isolated yields by column chromatography.



Scheme 3. Ullmann reaction mediated by Catalysts.



Scheme 4. Effect of base on Ullmann reaction mediated by catalyst **2**.

Table 3. Effect of base on catalyst **2** in Ullmann reaction.

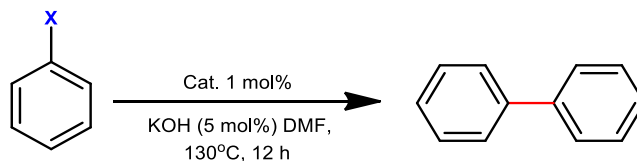
Entry	Base (5 mol%)	Isolated Yield (%) ^[a]
1	KOH	85
2	K ₂ CO ₃	67
3	Cs ₂ CO ₃	50
4	KOAc	49
5	NaOH	55

[a] Isolated yields by column chromatography.

reactions were studied using only ligands (**L¹H** and **L²H**) as organocatalysts (Table 2, entries 7 and 8). As reported in entries 9 and 10 (Table 2), the Ullmann reaction was carried out using one mol% of *in situ* silver nitrate and copper nitrate with corresponding imidazolium carboxylate ligands (**L¹H** and **L²H**) in the presence of five mol% potassium hydroxide. However, the yield of entries 1–10 were not appreciable compared to catalysts **1** and **2** (Table 2, entries 11 and 12). Although, the catalysts **1** and **2** are very active, **2** gave excellent conversion for iodobenzene (Yield, 85%) (Table 2, entry 12).

In order to understand the choice of base, we investigated the catalytic reaction with different bases in DMF (Scheme 4). KOH (Table 3, entry 1) was found to be more effective than other bases such as K₂CO₃, Cs₂CO₃, KOAc and NaOH (Table 3, entries 2–5). Subsequently, we investigated the scope and the generality of the method under the optimized reaction conditions. Thus, the optimized condition for the Ullmann reaction is reported in Scheme 5. We have investigated the reactions using aryl iodide, aryl bromide and aryl chloride. The results are summarized in Table 4. Catalyst **2** is highly active for iodobenzene (Table 4, entry 2), while bromobenzene (Table 4, entry 4) and chlorobenzene (Table 4, entry 6) gave considerable yield.

The catalytic efficiency of **2** is comparable with the copper catalyst in Ullmann coupling.¹⁴ However silver(I)-mediated Ullmann reaction is rare. As reported^{1,5,14} silver(I) is expected to mediate the reaction through red-ox mechanism. The catalyst **1**-mediated Ullmann reaction yield is nearly comparable with copper(II)-mediated reaction.¹⁴ Although, the mechanism of catalyst **1** or **2**-mediated Ullmann



Scheme 5. Evaluation of catalytic scope of **1** and **2**.

Table 4. Evaluation of catalytic scope of **1** and **2**.

Entry	Substrate	Catalyst (1 mol%)	Isolated Yield (%) ^[a]
1	Iodobenzene	1	58
2	Iodobenzene	2	85
3	Bromobenzene	1	55
4	Bromobenzene	2	70
5	Chlorobenzene	1	49
6	Chlorobenzene	2	62

[a] Isolated yields by column chromatography.

reaction is unclear at this stage, the active centre should be metal centre (See Table 2, entries 2–6 and 9–10 vs entries 7–8). Besides, the significant role of imidazolium carboxylate ligand in the catalytic process cannot be ignored (See Table 2, entries 9–12).⁷

4. Conclusions

In conclusion, we investigated the first catalytic application of imidazolium carboxylate supported silver(I) and copper(II) assemblies for Ullmann coupling. We have also demonstrated novel structural topologies and versatile coordination properties of coordination polymers by tuning the number of flexible node at organic spacer, and employing judicious synthetic strategies. The catalysts **1** and **2** show efficient homocoupling of aryl halide reactions to generate the corresponding diaryl products in excellent yields. Their catalytic applications in Ullmann reactions have shown wide scope with different halobenzenes. Structural insights into these compounds provide an explanation for the diverse catalytic behaviour of these compounds. Future studies on the reactivity of these ligands and their coinage metal complexes toward Ullmann cross coupling (N/O-arylation) are underway in our laboratory.

Supplementary Information (SI)

CCDC 1496983-1496984 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or by

email: deposit@ccdc.cam.ac.uk. Figures S1–S8 are available in Supplementary Information at www.ias.ac.in/chemsci.

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