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Copper(II) complexes of a heterotopic *N*-heterocyclic carbene ligand: Preparation and catalytic application

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Copper complexes containing a *N*-heterocylic carbene (NHC)/amidate/pyridine tridentate, 3-mesityl-1-(2-oxo-2-[{pyridin-2-ylmethyl}amino]ethyl)-imidazolin-2-ylidene (**HL**), were synthesized and characterized. By X-ray single crystal analysis, both Cu(**L**)(OAc) (**3a**) and Cu(**L**)Br (**3b**) show that the metal center is coordinated by a CNN-tridentate and a anionic donor in a slightly distorted square-planar geometry. These copper complexes are active as catalysts for oxidative bromination of dimethoxybenzene and styrene with the use of LiBr as the bromine source and oxygen as the terminal oxidant.

1. Introduction

Complexes with a multiple dentate containing a combination of disparate donor atoms are believed to exhibit unusual properties as each donor will give variable influence to the metal center. Among various donors, *N*-heterocyclic carbenes (NHC) have received considerable attention due to their strong σ donor ability and stability. Thus, the use of NHC as the primary donor in the heterotopic multi-dentates is a good ligand design and numerous systems are reported [1]. On the other hand, amidate ligands, showing a different donating property from NHC, have been used as a modular set for early transition-metal complexes [2]. In surveying the literature, only few heterotopic dentates containing both NHC and amidate donors have appeared [3–6] and Scheme 1 shows few known NHC-based tridentates containing an amidate donor [4–6]. Amidate donors in these NHC-based tridentate not only increase the chemically stability of metal complexes and also provide a good catalytic activity on the oxidative boron Heck-type reactions of aryl boronic acids with alkenes [4c]. In this work we aimed to study the coordination behavior of a heterotopic tridentate **HL** containing NHC/amidate/pyridine donors toward Cu(II) ions and their catalytic activity.

2. Results and discussion

2.1. Preparation and characterization of complexes

The preparation of the desired carbene precursor **2** is quite straightforward (Scheme 2). Alkylation of *N*-mesitylimidazole with ethyl α-bromoacetate gave the imidazolium salt **1**, which was subsequently treated with 2-picolylamine to provide the amide-linkage product **2**. Treatment of **2** with Ag_2O followed by $Cu(OAc)_2$ rendered the desired copper complex **3a** as purple solids in 78% yield. Similarly, the bromide analog **3b** was obtained by the reaction of **2** with Ag_2O followed by the treatment of $CuBr_2$.

Ligand **2** has been fully characterized by spectroscopic methods. ESI-MS spectrum of **2** shows *m*/*z* at 335.17, which is consistent with the formula of $C_{20}H_{23}N_4O$ [M-Br]. Absorptions at 1689 cm^{-1} in the IR spectrum is the characteristic stretching frequency for C=O of the amido moiety, whereas the ^1H nmr spectrum of **2** in dmso-d_6 shows signals at $\delta = 9.53$ (1H), 5.31 (2H) and 4.47 (2H) corresponding to the protons of the C-2 imidazolium, methylene unit adjacent to carbonyl and methylene unit attached to pyridinyl ring, respectively. These data are consistent to the structure of **2**.

Deprotonation of imidazolium salt **2** with a strong base, expecting to produce the corresponding free carbene, unfortunately failed presumably due to the interference from the deprotonation of the amido proton. Alternatively, the imidazolium salt was converted into its silver carbene complex *via* the reaction of **2**

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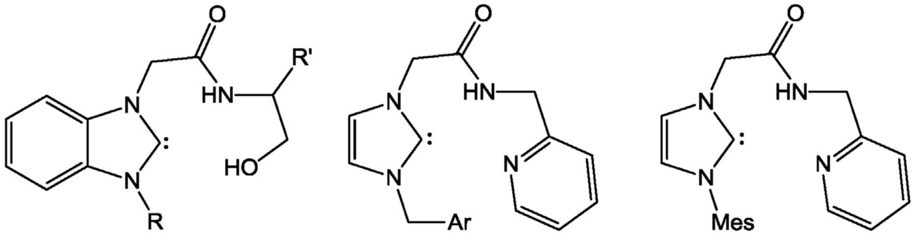
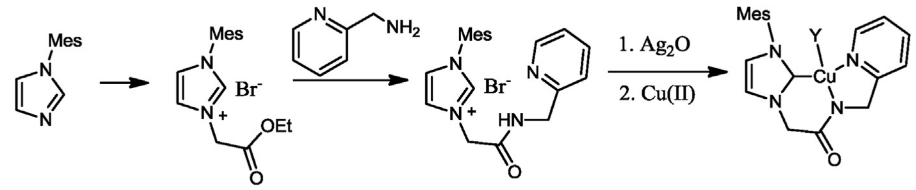


HL (this work)

Scheme 1. NHC-based tridentate containing an amidate donor.



1 **2** **3a** Y = OAc **3b** Y = Br

Scheme 2. Preparation of copper(II) complexes.

with Ag_2O in acetonitrile. Without further purification, the silver complex was subjected to undergo the carbene transfer reaction with $Cu(OAc)_2$. The desired copper carbene complex **3a** was obtained as dark purple solid in 78% yield, whereas carbene transfer reaction with $CuBr_2$ gave **3b** as yellowish green solid in 70% yield.

Due to the paramagnetic nature of Cu(II), the ^1H nmr spectrum of **3a** shows broaden signals, giving no information about the structure. Infrared spectra of **3a** show distinctive absorptions at 1587 and 1565 cm^{-1} in solid state as well as 1592 and 1569 cm^{-1} in $CHCl_3$, which are assigned to the carbonyl stretching of the amido moiety and the coordinating acetate ligand, respectively. Comparing to the free ligand, the carbonyl stretching frequency of the amido group in **3a** appears a dramatic shift, indicating the coordination of amido moiety toward the metal center. Absorption spectrum of **3a** in MeOH exhibits three signals at 220 ($\varepsilon = 7.2 \times 10^3$), 256 ($\varepsilon = 4.2 \times 10^3$), 340 (sh, $\varepsilon = 2.4 \times 10^2$) and 602 ($\varepsilon = 40$) nm^{-1}. The weak broad band around 602 nm is due to d-d transition of copper(II) complexes in a tetrahedrally square planar geometry [7]. As for **3b**, electronic absorptions at 219, 250, 340 (sh) and 640 nm and the carbonyl stretching frequency at 1595 cm^{-1} are quite similar to those for **3a**, indicating a similarity of coordination environment between two species. The μ_{eff} values of the bulk solids of **3a** and **3b** were found to be 1.43 and 1.71 μ_B at 295 K, respectively, which are close to the spin value for d^9-systems. Nevertheless, both structures are confirmed by X-ray crystallography.

Crystals of **3a-b** suitable for X-ray diffraction analysis were obtained by slow diffusion of Et_2O into a saturated solution of the complex in *N,N*-dimethylformamide. Selected key bond distances and angles are summarized in Table 1, while ORTEP plot for **3a** and **3b** are illustrated in Figs. 1 and 2, respectively.

In both complexes, the copper atom displays a distorted square-planar geometry with the coordination of a pyridine-imidazolinylidene-amidate tridentate and a terminal acetate in **3a** or a bromide in **3b**. The bond lengths of the Cu atom and the carbene carbon [Cu(1)-C(10)] are 1.962(3) Å in **3a** and 1.941(4) Å in **3b**, respectively, which are typical for such bonding. The distance of Cu(1)-N(3) is slightly shorter than that of Cu(1)-N(4), showing a stronger donating ability of the amidate ligand versus the pyridinyl nitrogen donor. The angle of N(3)-Cu(1)-N(4) (around 82°) deviating from 90° is presumably due to the geometrical constraint of

Table 1
Selected bond distances (Å) and bond angles (deg) for **3a** and **3b**.

Complex	3a, X = O(2)	3b, X = Br(1)
Cu(1)-C(10)	1.962(3)	1.941(4)
Cu(1)-X	1.989(2)	2.3874(6)
Cu(1)-N(3)	1.947(2)	1.942(3)
Cu(1)-N(4)	2.005(3)	2.016(3)
C(14)-O(1)	1.240(4)	1.244(4)
C(14)-N(3)	1.330(4)	1.329(5)
C(10)-Cu(1)-N(3)	92.29(12)	92.09(14)
N(3)-Cu(1)-N(4)	82.03(11)	82.3(12)
N(4)-Cu(1)-X	90.28(10)	95.79(9)
X-Cu(1)-C(10)	99.67(11)	97.92(10)
C(10)-Cu(1)-N(4)	162.80(12)	158.88(15)
N(3)-Cu(1)-X	161.14(11)	154.25(11)

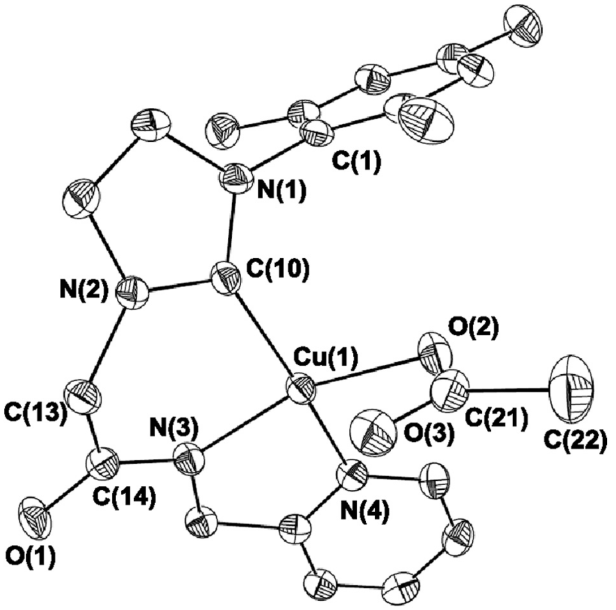


Fig. 1. ORTEP plot of **3a** (30% probability ellipsoids).

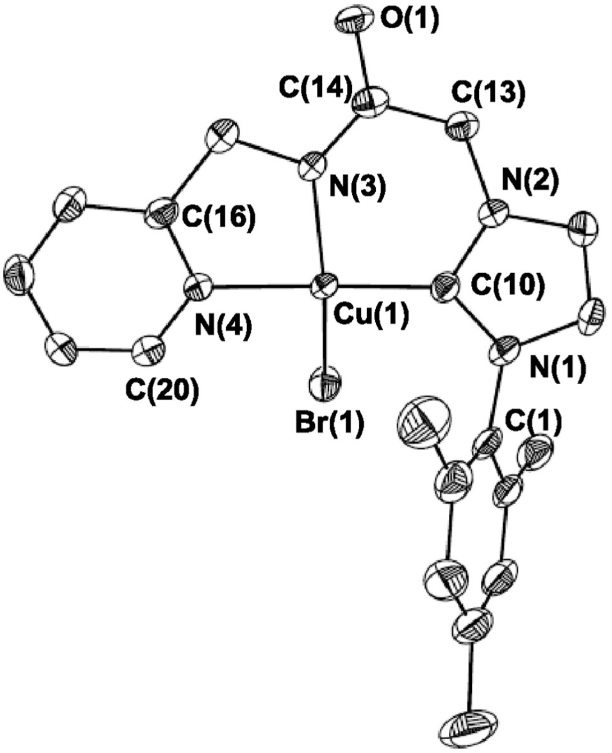


Fig. 2. ORTEP plot of **3b** (30% probability ellipsoids).

the chelation. It is noticed that the distance between Cu(1) and O(3) in complex **3a** is 2.574(3) Å, indicating a weak interaction. No significant discrepancies in other bond lengths and angles are noticed in complexes **3a** and **3b**.

2.2. Catalytic bromination of styrene

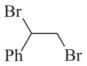
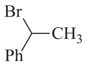
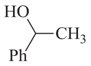
Due to the low cost and the diverse redox property of copper metal ions, the use of copper compounds as catalysts in oxidation reactions has received much attention. NHC-copper catalysts have provided good level of activity in oxidation of arenes [8]. On the other hand, the use of halide ions as a halogen source together with a suitable oxidant for the halogenation of organic substrates is a more attractive method due to the ecologically benign. Among various oxidant, the use of O_2 as the terminal oxidant ought to be the best choice. Thus, we investigated the catalytic activity of **3a** in bromination of styrene and arenes with the use of LiBr as the bromine source under molecular oxygen in this work. Bromination of styrene into 1,2-dibromostyrene was chosen to establish the optimized catalytic conditions.

A reaction of styrene with LiBr in the presence of CF_3COOH in acetonitrile gave the hydration and hydrobromination products as the major product, which is typical for the electrophilic addition (Table 2, entry 1). However, 1,2-dibromo-1-phenylethane, $PhCHBrCH_2Br$, became as the major product upon the addition of complex **3a** in the presence of oxygen atmosphere (Table 2, entry 2), indicating that the copper complex readily assisted the formation of the brominating agent, i. e. the oxidation of bromide took place. By increasing the amount of CF_3COOH or different acids, the hydration pathway always competes with the dibromination (entries 3–8). To our delight, the dibromination product was obtained exclusively by running the reaction in a nitromethane solution (entry 10). Other solvents provide the less satisfactory results. According to the reaction mechanism proposed by Stahl's and coworkers (Scheme 3), disproportionation of $CuBr_2$ would provide the molecular bromine [9], which is for the electrophilic addition of C=C. The Cu(I) intermediate could be then oxidized to regenerate Cu(II) species under acidic conditions. Therefore, the catalytic amount of **3a** responses for the generation of the brominating agent for the reaction.

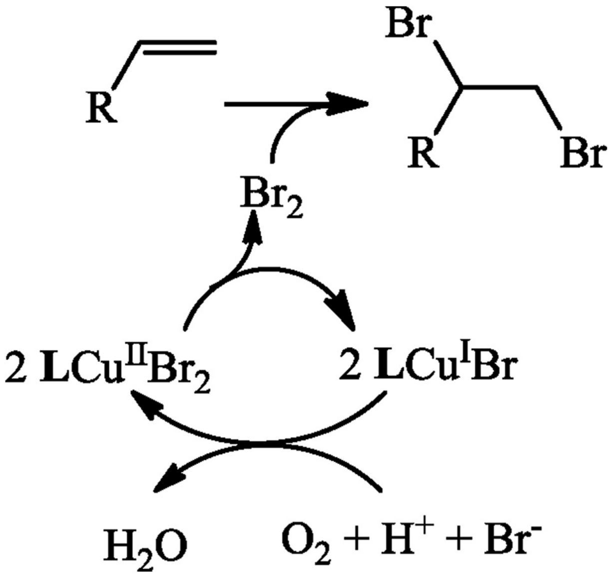
To examine the activity of **3a** for monitoring reaction progress in real time, the bromination of styrene catalyzed by **3a** was performed and the amount of products were analyzed by ^1H NMR spectroscopy (Fig. 3). At the beginning of the reaction, styrene was consumed rapidly to form $PhCHBrCH_3$ majorly with a small amount of $PhCHBrCH_2Br$. However, as the reaction proceeded, the concentration of $PhCHBrCH_3$ was slowly decreased and converted into $PhCHBrCH_2Br$ and eventually reached 100% yield of dibromination product in 16 h. In a separated experiment, without the presence of Cu(II) catalyst, we found that styrene was converted into $PhCHBrCH_3$ *via* hydrobromination under this reaction condition. Thus, the pathway of this reaction is proposed in Scheme 4.

Initially, styrene was hydrobrominated to yield $PhCHBrCH_3$. This step is a reversible reaction and styrene is able to re-generate *via* an E_1 elimination. In the meantime, styrene was converted into the $PhCHBrCH_2Br$ as the brominating agent was generated *in situ* by the

Table 2
Bromination of styrene catalyzed by **3a** with LiBr as bromine source.[a]

entry	LiBr (mmol)	Acid (mmol)	Solvent	Conv. (%)	Yields (%)[b]		
							
1[c]	4.0	CF_3CO_2H (1.6)	CH_3CN	98	–	36	60
2	4.0	CF_3CO_2H (1.2)	CH_3CN	96	47	28	20
3	4.0	CF_3CO_2H (1.6)	CH_3CN	100	83	–	15
4	4.0	CF_3CO_2H (2.0)	CH_3CN	100	72	13	12
5	2.0	CF_3CO_2H (2.0)	CH_3CN	100	60	12	11
6	4.0	H_3PO_4 (0.4)	CH_3CN	95	27	29	35
7	4.0	H_3PO_4 (1.2)	CH_3CN	97	31	25	38
8	4.0	H_2SO_4 (0.4)	CH_3CN	95	42	26	24
9	4.0	CF_3CO_2H (1.6)	CH_3NO_2	100	91	7	0
10	4.0	CF_3CO_2H (1.2)	CH_3NO_2	100	98	–	–
11	4.0	CF_3CO_2H (1.6)	dioxane	94	40	–	–
12	4.0	CF_3CO_2H (1.6)	toluene	100	17	80	–
13	4.0	CF_3CO_2H (1.6)	acetone	86	–	75	
14	4.0	CF_3CO_2H (1.6)	DMF	71	63	–	–

[a] Reaction conditions: styrene (0.4 mmol), LiBr, **3a** (0.02 mmol, 5 mol%) and acid in solvent (1 mL) under O_2 (1 atm) at 60 °C for 20 h.
[b] NMR yields.
[c] No catalyst.



Scheme 3. Catalytic pathway for bromination of C=C.

Cu(II) catalyst. However, the bromination of C=C is an irreversible process. Thus, $PhCHBrCH_2Br$ becomes the final product upon a prolong treatment. The addition of bromine toward double bond under this catalytic system was also evidenced by the other substrate. Under the optimized condition, cyclohexene was transferred into *trans*-1,2-dibromocyclohexane directly within 4 h. No cyclohexyl bromide was detected during the reaction, i.e. hydrobromination does not occur with cyclohexene and the addition of bromine to C=C takes place directly.

We also evaluated the activity of various copper complexes for the bromination of styrene under the optimal conditions (Table 3). It is noticed that both complexes **3a** and **3b** have the similar activity, as expected. Quite a number of Cu(II) complexes do exhibit some catalytic activity on the generation of "Br_2", but not as good as complexes **3a-b**, indicating that the designed ligand does assist the metal ions in generation of bromine for the addition of C=C.

2.3. Catalytic bromination of m-dimethoxybenzene

The experimental reaction condition of the bromination of *m*-dimethoxybenzene (Scheme 5) was based on the study by Stahl in a similar reaction [9]. A mixture of *m*-$(MeO)_2C_6H_4$, LiBr and **3a** (5 mol %) in acetic acid under atmospheric pressure of O_2 was heated at 60 °C for 24 h (Table 4). The mono-brominated product **4** was obtained (Table 4, entries 1–4) in various amount under different reaction parameters. The condition providing the best yield is carrying out the reaction with the use of 4 equiv. molar of LiBr at 100 °C, however, with a small amount of the dibromination product **5** (entry 4).

Despite this optimization, we further examined other optimized conditions. Instead of using acetic acid as the solvent, acetonitrile was chosen as the solvent for the further investigation. By manipulating the amount of CF_3COOH and LiBr, compound **4** was still obtained as the major product, but not as good as the above optimized condition (Table 4, entries 5–8). According to the reaction mechanism for this halogenation proposed by Stahl's work (Scheme 3), the regeneration of Cu(II) species proceeds under acidic conditions. Inspired by this hint, we screened various acids for this catalysis to examine such effect (entries 9–14). To our delight, the desired mono-bromination product **4** could be obtained almost quantitatively with the use of sulfuric acid and 1.5 equivmolar of LiBr (entry 11). Based on this condition, solvent effect was then examined (entries 15–19) and acetonitrile was the best choice for this catalysis. After these investigation, the standard reaction conditions were determined to be: 5 mol% of **3a**, 1.5 equivalents of LiBr and 1 equivalent of H_2SO_4 in acetonitrile at 70 °C under an oxygen atmosphere for 24 h (Table 4, entry 11).

A series of experiments was carried out to evaluate the ability of various copper complexes for the bromination under the optimized conditions for comparison (Table 5). Some copper complexes

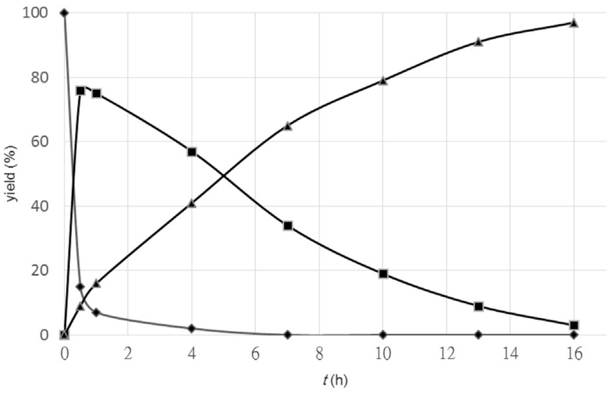
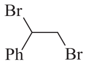
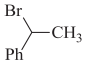
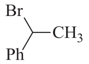
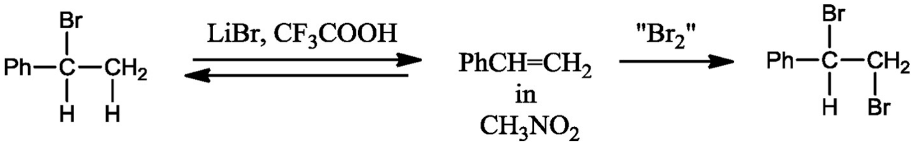


Fig. 3. Catalytic bromination of styrene with LiBr [Reaction conditions: styrene (0.6 mmol), LiBr (6 mmol), TFA (1.8 mmol) and **3a** (0.03 mmol) in CH_3NO_2 (1.5 mL) at 60 °C under O_2 atmosphere (1 atm). (◆) $PhCH=CH_2$, (■) $PhCHBrCH_3$, (▲) $PhCHBrCH_2Br$.

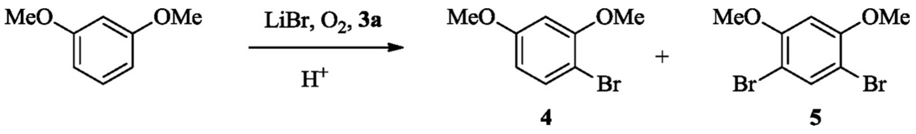
Table 3
Activity of various Cu(II) complexes in bromination of styrene.[a]

Entry	Catalyst			
1	Complex **3a**	98%	–	–
2	Complex **3b**	100%	–	–
3	$CuBr_2$	67%	27%	–
4	$(Py)_2CuBr_2$	57%	39%	–
5	$(Py)_4CuBr_2$	69%	27%	–
6	$(PMDETA)CuBr_2$	22%	73%	–
7	$(bpy)CuBr_2$	20%	70%	–
8	$[(bpy)_2CuBr]Br$	30%	64%	–
9	$[(phen)_2CuBr]Br$	9%	84%	–
10	$[(phen)CuBr]_2$	29%	69%	–
11	$(tpy)CuBr_2$	20%	75%	–
12	No Cu complex	–	84%	11%

[a] Condition: styrene (0.4 mmol), LiBr (4.0 mmol), CF_3CO_2H (1.2 mmol) and Cu complex (5 mol%) in CH_3NO_2 (1 mL) at 60 °C for 20 h, yields of products were determined by ^1H NMR spectroscopy.



Scheme 4. Pathway of catalytic bromination of styrene.



Scheme 5. Bromination of arene catalyzed by **3a.**

exhibited good activity for this electrophilic aromatic bromination (Table 5, entries 3–6). By shortening the reaction to 12 h, both complex **3a** and **3b** prove to be superior to other copper complexes (Table 5, entries 12–17), indicating a ligand effect on the catalysis. The turnover number for **3a** is about 20 mol(product)/mol(catalyst), which is higher than other reported works [9].

3. Summary

In this work, we have synthesized and characterized Cu(II) complexes with a tridentate with NHC/amidate/pyridine donors. Coordination geometry of both copper complexes **3a** and **3b** is in a slightly distorted square-planar geometry as demonstrated by single crystal and spectroscopic analyses. These copper complexes are active catalysts for bromination of styrene and dimethoxybenzene with the use of LiBr as the bromine source and the oxygen as the final oxidant. The study proves that the designed ligand does assist the copper center in generating the brominating agent for organic substrates. Compared to the literature work, the copper complexes **3a** and **3b** appear to be excellent catalysts, which makes this process potentially useful for synthetic application.

4. Experimental section

4.1. Methods and materials

General information. Chemicals and solvents were of analytical grade and used without further purification. Nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. *N*-mesitylimidazole was prepared according to the literature method [10]. Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS-3 SQUID instrument operating at a magnetic field of 0.1 T between 2 and 300 K.

4.2. Synthesis and catalysis

4.2.1. Preparation of 3-(2-ethoxy-2-oxoethyl)-1-mesityl-1H-imidazole-3-ium bromide (1)

A mixture of 1-mesitylimidazole (3.2 g, 17 mmol) and ethyl bromoacetate (3.5 g, 20 mmol) in anhydrous acetonitrile (40 mL)

Table 5
Comparison of activity of various Cu(II) complexes.[a]

entry	Catalyst[b]	Conv.	Yield[c] of 4	Yield[c] of 5
1	**3a**	100%	95%	4%
2	**3b**	100%	80%	18%
3	$CuBr_2$	87%	85%	–
4	$(Py)_2CuBr_2$	94%	90%	–
5	$(Py)_4CuBr_2$	100%	95%	–
6	$(PMDETA)CuBr_2$	86%	84%	–
7	$(bpy)CuBr_2$	74%	72%	–
8	$[(bpy)_2CuBr]Br$	60%	58%	–
9	$[(phen)_2CuBr]Br$	35%	34%	–
10	$[(phen)CuBr]_2$	51%	49%	–
11	$(tpy)CuBr_2$	62%	62%	–
12[d]	**3a**	99%	98%	–
13[d]	**3b**	100%	100%	–
14[d]	$CuBr_2$	65%	64%	–
15[d]	$(Py)_2CuBr_2$	80%	78%	–
16[d]	$(Py)_4CuBr_2$	79%	79%	–
17[d]	$(PMDETA)CuBr_2$	73%	73%	–

[a] Conditions: $m-C_6H_4(OMe)_2$ (0.3 mmol), LiBr (0.45 mmol), Cu complex (5 mol%) and H_2SO_4 (0.3 mmol) in CH_3CN (0.5 mL) at 70 °C for 24 h.
[b] PMDETA= *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; bpy = bipyridine; phen = 1,10-phenanthroline.
[c] NMR yields.
[d] Running the reaction for 12 h.

Table 4
Optimization for the bromination of $m-C_6H_4(OMe)_2$.[a]

entry	LiBr (mmol)	Acid	solvent	T (°C)	Conv. (%)	Yield (%)[b]	
						4	5
1	0.6	CH_3COOH	CH_3CO_2H (1 mL)	60	47	46	–
2	1.2	CH_3COOH	CH_3CO_2H (1 mL)	60	63	62	–
3	1.2	CH_3COOH	CH_3CO_2H (1 mL)	80	68	66	–
4	1.2	CH_3COOH	CH_3CO_2H (1 mL)	100	100	92	6
5	1.2	CF_3CO_2H (1.5 mmol)	CH_3CN (0.5 mL)	70	100	67	30
6	0.6	CF_3CO_2H (1.5 mmol)	CH_3CN (0.5 mL)	70	100	87	11
7	0.45	CF_3CO_2H (1.5 mmol)	CH_3CN (0.5 mL)	70	100	84	13
8	0.3	CF_3CO_2H (1.5 mmol)	CH_3CN (0.5 mL)	70	83	83	–
9	1.2	H_2SO_4 (0.3 mmol)	CH_3CN (0.5 mL)	70	100	60	35
10	0.6	H_2SO_4 (0.3 mmol)	CH_3CN (0.5 mL)	70	100	85	14
11	**0.45**	**H_2SO_4 (0.3 mmol)**	**CH_3CN (0.5 mL)**	**70**	**100**	**95**	**4**
12	0.3	H_2SO_4 (0.3 mmol)	CH_3CN (0.5 mL)	70	72	71	–
13	1.2	H_3PO_4 (0.6 mmol)	CH_3CN (0.5 mL)	70	83	81	–
14	1.2	CH_3CO_2H (1.5 mmol)	CH_3CN (0.5 mL)	70	18	17	–
15	0.45	H_2SO_4 (0.3 mmol)	CH_3NO_2 (0.5 mL)	70	100	70	8
16	0.45	H_2SO_4 (0.3 mmol)	dioxane (0.5 mL)	70	100	82	–
17	0.45	H_2SO_4 (0.3 mmol)	toluene (0.5 mL)	70	33	27	–
18	0.45	H_2SO_4 (0.3 mmol)	DMF (0.5 mL)	70	38	30	–
19	0.45	H_2SO_4 (0.3 mmol)	CH_3OH (0.5 mL)	70	56	53	–

[a] Reaction conditions: $m-C_6H_4(OMe)_2$ (0.3 mmol), LiBr, **3a** (5 mol%) and acid in solvent under O_2 (1 atm) for 24 h.
[b] NMR yields.

was heated to reflux for 40 h. After removal of solvents, the residue was re-precipitated from methanol/ether 3 times. The desired compound **1** was obtained as light-yellow solids (5.33 g, 89%): ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.47 (s, 1H), 8.05 (s, 1H), 7.96 (s, 1H), 7.16 (s, 2H), 5.38 (s, 2H), 4.26 (q, $J = 8.0$ Hz, 2H), 2.33 (s, 3H), 2.02 (s, 6H), 1.25 (t, $J = 6$ Hz, 3H); ^{13}C NMR (100 MHz): δ 167.34, 141.03, 139.61, 134.91, 131.73, 129.98, 125.17, 124.10, 62.70, 50.65, 21.30, 17.54, 14.64. IR ($CDCl_3$) $\upsilon_{(C=O)}$ 1750 cm^{-1}.

4.2.2. *Preparation of ligand (**2**)*

A mixture of **1** (2 g, 5.7 mmol) and 2-picolylamine (0.9 g, 8.5 mmol) in ethanol (40 mL) was stirred at 60 °C for 65 h. After removal of ethanol, the residue was re-precipitated from methanol/ether 3 times to yield yellow solids (2.13 g, 90%): ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.53 (s, 1H), 9.28 (t, $J = 4$ Hz, 1H), 8.52 (d, $J = 4$ Hz, 1H), 8.09 (s, 1H), 7.94 (s, 1H), 7.78 (t, $J = 8$ Hz, 1H), 7.43 (d, $J = 8$ Hz, 1H), 7.30 (t, $J = 6$ Hz, 1H), 7.14 (s, 2H), 5.31 (s, 2H), 4.47 (d, $J = 4$ Hz, 2H), 2.32 (s, 3H), 2.03 (s, 6H); ^{13}C NMR (100 MHz): δ = 165.8, 158.3, 149.6, 140.9, 139.6, 137.5, 135.0, 131.8, 129.9, 125.3, 123.8, 123.1, 122.0, 51.7, 45.2, 21.3, 17.6. IR ($CDCl_3$) $\upsilon_{(N\text{-}H)}$ 3214 and $\upsilon_{(C=O)}$ 1689 cm^{-1}. ESI-MS: *m/z* [M-Br] Calcd. for $C_{20}H_{23}N_4O$: 335.18, Found: 335.17.

4.2.3. *Preparation of complex **3a***

A mixture of **2** (0.3 g, 0.72 mmol) and Ag_2O (0.1 g, 0.43 mmol) in a 50 mL flask was flashed with nitrogen gas. Anhydrous acetonitrile (10 mL) was syringed into the flask. The resulting solution was stirred at 65 °C for 20 h. $Cu(OAc)_2 \cdot H_2O$ (0.15 g, 0.72 mmol) was added to the above solution and stirred for another 20 h. The reaction mixture was filtered through Celite and ether was added to the filtrate to yield the desired complex **3a** as purple solids (256 mg, 78%). IR (KBr) $\upsilon_{(C=O)}$ 1587 and 1565 cm^{-1}; IR ($CHCl_3$) $\upsilon_{(C=O)}$ 1592 and 1569 cm^{-1}. UV–Vis (MeOH) λ_{max} (ε): 220 ($\varepsilon = 7.2 \times 10^3$), 256 ($\varepsilon = 4.2 \times 10^3$), 340 (sh, $\varepsilon = 2.4 \times 10^2$) and 602 ($\varepsilon = 40$) nm^{-1}; $\mu_{eff} = 1.43$ μ_B (295 K); HRMS (ESI): *m/z* 396.1007 [M-OAc]$^+$, calcd. 396.1017.

4.2.4. *Preparation of copper complex **3b***

A mixture of **2** (55 mg, 0.13 mmol) and Ag_2O (18.5 mg, 0.08 mmol) in a 5 mL flask was flashed with nitrogen. Anhydrous acetonitrile (1.5 mL) was added and the resulting mixture was heated at 65 °C for 20 h. $CuBr_2$ (29.5 mg, 0.13 3 mmol) and K_2CO_3 (18.3 mg, 0.13 mmol) was added to the above solution. After stirring for another 20 h, the mixture was filtered through Celite. The filtrate was concentrated and the residue was re-precipitated from acetonitrile/ether to give dark purple solids (240 mg, 70%). IR ($CHCl_3$) $\upsilon_{(C=O)}$ 1595 cm^{-1}. UV–Vis (MeOH) λ_{max} (ε): 219 (1.0×10^4), 250 (5.2×10^3), 340 (sh, 1.3×10^3), 381 (sh, 5.4×10^2) and 640 (79) nm; $\mu_{eff} = 1.71$ μ_B (295 K); HRMS (ESI): *m/z* 396.1088 [M-Br]$^+$, calcd. 396.1017.

4.2.5. *Catalytic bromination of styrene*

A mixture of styrene (0.4 mmol), LiBr (4.0 mmol), CF_3CO_2H (1.2 mmol) and Cu complex (5 mol%) in CH_3NO_2 (1 mL) was loaded in reaction tube and heated at 60 °C under oxygen atmosphere for 20 h. After the reaction, the yields were determined by ^{1}H NMR integration with the use of methylsulfone as the internal standard in $CDCl_3$.

4.2.6. *Catalytic bromination of m-dimethoxybenzene*

A reaction flask was loaded with *m*-$(MeO)_2C_6H_4$ (0.3 mmol), LiBr (0.45 mmol), Cu complex (5 mol%) and H_2SO_4 (0.3 mmol) in CH_3CN (0.5 mL). The mixture was heated at 70 °C under oxygen atmosphere for 24 h. The product yields were determined by ^{1}H NMR integration with the use of methylsulfone as the internal standard in $CDCl_3$.

4.3. *X-ray crystallographic analysis*

Crystals suitable for X-ray determination were obtained for **3a-b** by slow diffusion of ether into a DMF solution at room temperature. Cell parameters were determined by a Siemens SMART CCD diffractometer. Crystal data **3a**: $C_{22}H_{24}CuN_4O_3$, $F_w = 455.99$, Triclinic, P-1, $a = 8.9332(6)$ Å, $b = 9.1999(3)$ Å, $c = 13.6399(5)$ Å, $\alpha = 100.225(3)^o$, $\beta = 107.748(5)°$, $\gamma = 93.324(4)°$, $V = 1043.14(9)$ Å^3, Z = 2, $D_{calcd} = 1.452$ Mg/m^3, $F(000) = 474$, crystal size: $0.20 \times 0.15 \times 0.10$ mm^3, 3.30 to 25.00°, 6176 reflections collected, 3646 reflections [R(int) = 0.0311], Final R indices [I > 2sigma(I)]: R1 = 0.0445, wR2 = 0.1105, for all data R1 = 0.0527, wR2 = 0.1198, Goodness-of-fit on $F^2 = 1.078$. Crystal data **3b**: $C_{20}H_{21}BrCuN_4O.0.5(C_4H_{10}O)$, $F_w = 513.92$, Monoclinic, P2(1)/n, $a = 8.1841(4)$ Å, $b = 21.3054(7)$ Å, $c = 12.8818(4)$ Å, $\alpha = 90°$, $\beta = 91.838(3)°$, $\gamma = 90°$, $V = 2244.99(15)$ Å^3, Z = 4, $D_{calcd} = 1.521$ Mg/m^3, $F(000) = 1048$, crystal size: $0.20 \times 0.15 \times 0.10$ mm^3, 3.14 to 25.00°, 8012 reflections collected, 3933 reflections [R(int) = 0.0370], Final R indices [I > 2sigma(I)]: R1 = 0.0416, wR2 = 0.0873, for all data R1 = 0.0629, wR2 = 0.0990, Goodness-of-fit on $F^2 = 1.028$. The structure was solved using the SHELXS-97 program [11] and refined using the SHELXL-97 program [12] by full-matrix least-squares on *F*2 values.

5. Supplementary data

CCDC 1579378 and 1579379 contain the supplementary crystallographic data for complexes **3a** and **3b**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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