



## Journal Name

COMMUNICATION

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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† Electronic Supplementary Information (ESI) available: [characterization data, optimization studies. See DOI: 10.1039/x0xx00000x]

**Design and application of diimine-based copper(I) complexes in photoredox catalysis<sup>†</sup>**

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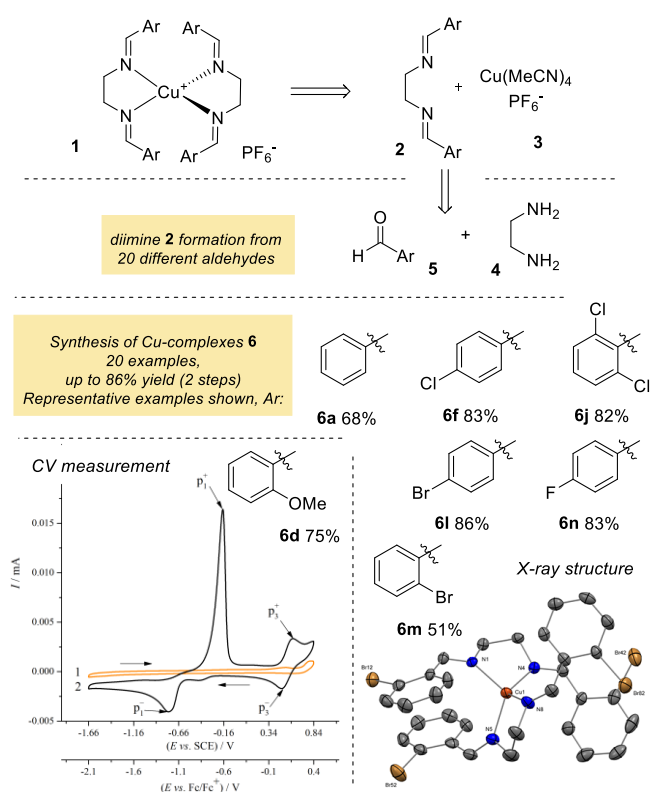
**Structurally different bis(imino)copper(I) complexes were prepared in a highly modular manner and utilized as copper-based photocatalysts in ATRA reactions of styrenes and alkyl halides. The new photocatalysts showed good catalytic activity and ensured efficient chemical transformations.**

Utilization of visible light-driven photocatalytic transformations in organic synthesis has become one of the most intensively investigated fields of organic chemistry.<sup>1</sup> In these photocatalytic reactions, an excited state photosensitizing dye generates a radical which can then take part in a catalytic cycle. One drawback of this synthetic technique is the use of expensive metal-based photocatalysts such as iridium and ruthenium complexes. Despite their high prices, these noble metals are used in a very broad area of synthetic chemistry.<sup>2</sup> In order to reduce the cost of these transformations, the change from noble metals to cheaper organic dyes is one direction of methodology developments in photoredox catalysis.<sup>3</sup> Bearing in mind the photochemical and redox properties there is opportunity to use cheaper transition metal complexes as sensitizers.<sup>4</sup> In this respect, copper is a promising candidate, and several successful applications of copper complexes were already reported in different areas of photochemistry.<sup>5</sup> Among the most active copper-based catalysts are phenanthroline complexes, such as homoleptic [Cu(dap)<sub>2</sub>]Cl (**1**,<sup>6</sup> Scheme 1), which shows impressive catalytic activity in photoredox transformations<sup>7</sup> such as addition of CBr<sub>4</sub>,<sup>6</sup> fluoroalkyl iodide,<sup>8</sup> aryl- and alkylsulfonyl,<sup>9</sup> and trifluoromethylsulfonyl chlorides<sup>10</sup> to styrenes or alkenes, intramolecular cyclization and difluoromethylation of alkenes,<sup>11</sup> intermolecular cyclization of *N*-phenylmaleimide with *N,N*-dialkylaniline<sup>12</sup> or azidation reactions.<sup>13</sup> It is worth mentioning that different heteroleptic copper complexes are also applicable as photocatalysts.<sup>14</sup>

Considering the structural features of these widely used excellent copper photocatalysts we aimed to design new bis-imine type *N,N* donor ligands and study the photocatalytic activity of their copper complexes in atom transfer radical addition (ATRA) reactions.<sup>15</sup> Our target diimines **2** can be easily prepared from ethylenediamine (**4**) and appropriate benzaldehydes (**5**) in ethanol at room temperature in a simple, efficient and highly modular manner. To build our ligand library, we used 20 different benzaldehyde derivatives containing F, Cl, Br, Ph, OMe, Me<sub>2</sub>N substituents

in *ortho*, *meta* and *para* positions. For the synthesis of copper complexes, two equivalents of ligand **2** were used with  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  and the desired catalysts (**6a–t**, representative examples are shown on Scheme 1) were isolated in excellent yields (up to 86% yield for two steps) by simple filtration after the addition of diethyl ether to the reaction mixture.<sup>16</sup> It is of note that, while some of these diimine ligands and their copper complexes have been reported previously<sup>17</sup> to our best knowledge only few copper complex of this type has been applied in a photocatalytic synthesis.<sup>18</sup>

The main bands of the absorption spectra can be characterized with considerable large oscillator strengths (see Figure S11), while the luminescence is very weak: the fluorescence yields are around  $10^{-5}$  and similarly to the shape of the spectra, slightly depend on the excitation wavelength. The main component of the singlet decay is very short, so we believe that most probably a triplet-like species induces the catalytic reaction. Using laser flash excitation transient absorption (TA) measurements a long-lived (30 ms) species can be detected at 460 nm, as well as the depletion of the ground state compound at 400 nm. Both observations indicate that the absorption spectrum of the long-lived triplet species is slightly shifted to the red with excitation. Even more, at presence of  $\text{CBr}_4$  a further kinetic increase of the TA signal may be observed at 460 nm



**Scheme 1** Design of new copper bis imine complexes.

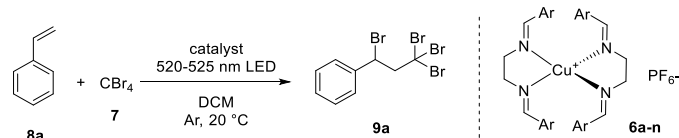
Cyclic voltammogram of **6d** (1) 100 mM TBABF<sub>4</sub> in MeCN and (2) 1 mM C<sub>36</sub>H<sub>40</sub>CuF<sub>6</sub>N<sub>4</sub>O<sub>4</sub>P (**6d**) / 100 mM TBABF<sub>4</sub> in MeCN.  $v = 50 \text{ mV}\cdot\text{s}^{-1}$ ;  $E = -1.73 - 0.77 \text{ V vs. SSCE}$ . The working electrode was a GC ( $A = 0.031 \text{ cm}^2$ ) plate.

with a characteristic time parameter of 100-200  $\mu\text{s}$  (see Figure SI2). The 30 ms time range would be enough for a bimolecular reaction, especially if one of the reactants makes a weak complex with the catalysts even at ground state.

The shape of the cyclic voltammograms recorded on glassy carbon and gold is significantly affected by the deposition-dissolution kinetics of Cu. A quasi-reversible peak couple can be observed at positive potentials, the  $E_{1/2}$  value varies between 0.49 V and 0.61 V vs. SCE.<sup>16</sup>

Complex **6m** was also characterized by single-crystal X-ray crystallography (Scheme 1).<sup>19</sup> The cation has C<sub>2</sub> symmetry and the ligands take a slightly twisted conformation around the central copper ion. The geometry around the Cu(I) centre is pseudotetrahedral. The large angular distortion is due to the small bite angle of the ligands ( $\text{N5-Cu1-N8} = 84.30^\circ$  and  $\text{N1-Cu1-N4} = 84.89^\circ$ ). Consequently, the interligand N-Cu-N angles are larger than those of a tetrahedral complex ( $\text{N1-Cu1-N5} = 114.94^\circ$ ,  $\text{N1-Cu1-N8} = 132.79^\circ$ ,  $\text{N4-Cu1-N5} = 133.76^\circ$ , and  $\text{N4-Cu1-N8} = 113.29^\circ$ , respectively). The angle of the CuN<sub>2</sub> planes is 72 degree and the average Cu-N distance is 2.035(5) Å while the average imine C-N bond distance is 1.27(1) Å. The C=N bonds show *trans* orientation. The average dihedral angle between the two phenyl rings of the same ligand molecule is 55.6° while the phenyl rings at the same side of the two ligands are close to parallel as the average dihedral angle is 5.0°. None the less, intramolecular  $\pi$ - $\pi$  stacking is unlikely as the two pairs of rings are substantially displaced laterally (average centroid distances are 5.2°).

**Table 1.** Optimization of reaction conditions<sup>a</sup>



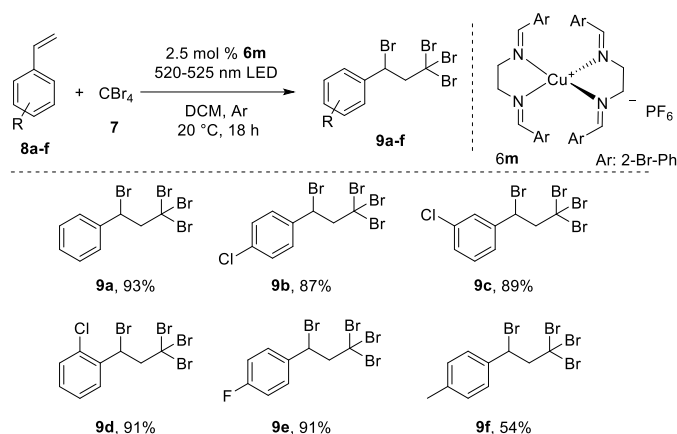
Entry	Catalyst	Ar (in <b>6</b> )	Cat. mol%	yield ( <b>9a</b> , %)
1	<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	1.0	23
2	<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	2.5	73
3	<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	1.0	0 <sup>b</sup>
4	<b>2a</b>	C <sub>6</sub> H <sub>5</sub>	2.0	0 <sup>c</sup>
5	Cu(MeCN) <sub>4</sub> PF <sub>6</sub>	-	3.0	0 <sup>d</sup>
6	<b>6a</b>	C <sub>6</sub> H <sub>5</sub> 4-	1.0	0 <sup>e</sup>
7	<b>6b</b>	Me <sub>2</sub> N- C <sub>6</sub> H <sub>4</sub> 4-	2.5	8
8	<b>6c</b>	MeO- C <sub>6</sub> H <sub>4</sub> 2-	2.5	53
9	<b>6d</b>	MeO- C <sub>6</sub> H <sub>4</sub> 2-Ph-	2.5	76
10	<b>6e</b>	C <sub>6</sub> H <sub>4</sub> 2-Ph-	2.5	88
11	<b>6f</b>	4-Cl- C <sub>6</sub> H <sub>4</sub>	2.5	62
12	<b>6g</b>	3-Cl- C <sub>6</sub> H <sub>4</sub>	2.5	79
13	<b>6h</b>	2-Cl- C <sub>6</sub> H <sub>4</sub> 2,4-	2.5	90
14	<b>6i</b>	Cl <sub>2</sub> - C <sub>6</sub> H <sub>3</sub>	2.5	83

15	<b>6j</b>	2,6- Cl <sub>2</sub> - C <sub>6</sub> H <sub>3</sub>	2.5	4
16	<b>6k</b>	2-F- C <sub>6</sub> H <sub>4</sub>	2.5	88
17	<b>6l</b>	4-Br- C <sub>6</sub> H <sub>4</sub>	2.5	88
18	<b>6m</b>	2-Br- C <sub>6</sub> H <sub>4</sub>	2.5	93
19	Cu(MeCN) <sub>4</sub> PF <sub>6</sub> + 2.5 % <b>2m</b>	-	2.5	41

<sup>a</sup> reaction conditions: 1 equiv. CBr<sub>4</sub>, catalyst, abs. DCM, argon atmosphere, rt, 18 hours, green LED. <sup>b</sup> in the dark (under Al foil). <sup>c</sup> only ligand **2a**. <sup>d</sup> only Cu(MeCN)<sub>4</sub>PF<sub>6</sub>. <sup>e</sup> without argon atmosphere.

With the series of complexes in hand, we first examined the photocatalytic activity of the copper catalysts in the atom transfer-radical addition (ATRA) of CBr<sub>4</sub> (**7**) to styrene (**8a**) as the chosen model reaction (Table 1).<sup>5k, 6</sup> During the optimization phase of the study, we examined the required catalyst loading of **6a**, and found that 2.5 mol% copper catalyst was necessary to reach full conversion of styrene in dichloromethane (DCM) in 18 hours, and **9a** was isolated in 73% yield (entry 2). When 1.0 mol% of copper photocatalyst was used, the yields of **9a** were significantly lower (entry 1). This finding shows slightly lower stability of the catalyst than the known [Cu(dap)<sub>2</sub>] complexes (catalyst loadings lower than < 1 mol% has been described). At this stage, we checked the catalytic effect of the copper catalyst and the importance of light irradiation. It was clearly demonstrated that there was no reaction in the absence of light or the copper complex (entries 3–5). It was also found that inert atmosphere is required for the successful addition (entry 6).

Next, an extended structure-activity relationship was carried out using different diimino copper complexes. The presence of electron donating (NMe<sub>2</sub>) group in *para* position of the aryl ring had deleterious effect on the yield compared to **6a** having an unsubstituted phenyl ring (entry 7). However, reaction with 4-methoxyphenyl derivative **6c** gave an acceptable 53% yield (entry 8).

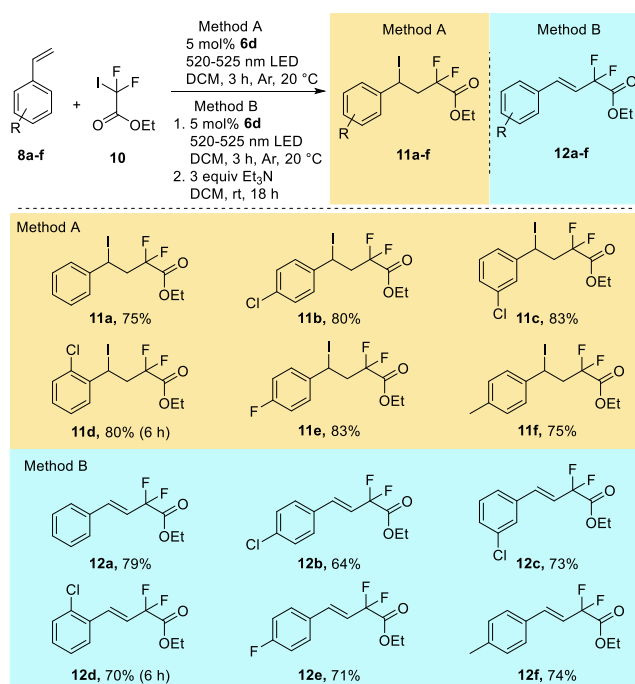


**Scheme 2** ATRA reactions of substituted styrene and carbon tetrabromide.

In order to enforce the pseudo-tetrahedral geometry around the Cu(I) centre, we prepared a series of complexes with *ortho* substituted aryl groups. Indeed, **6d** featuring *ortho* methoxy groups showed superior performance (76% yield, entry 9). The proof for the importance of the *ortho* substituent on the aryl rings led us to synthesize 2-biphenyl derivative **6e** having extended conjugation in the aromatic part. We found increased catalytic activity in case of **6e** and tetrabromo product **9a** was obtained in 88% yield (entry 10). The influence of the substituent position in the phenyl ring on the addition reaction was clearly observed in case of the chloro derivatives. The same trend was observed when the position of chlorine atoms was altered in complexes **6f**, **6g** and **6h**, and the reaction efficiency increased in the order of *para*-*meta*-*ortho* substituted ligands, and the adduct was isolated in 62%, 79% and 90% yield, respectively (entries 11–13). However, the occupation of both *ortho* positions of the phenyl rings had deleterious effect (4% yield, entry 15), presumably due to instability of complex **6j**, which was proved by electrochemical analysis.<sup>16</sup> To probe the importance of steric effects over electronic ones we performed the reaction with 2,4-dichloro derivative **6k** as catalyst, which provided the desired product in good 83% yield (entry 14). Besides Cl the presence of other halogen atoms such as F or Br in the ligand of the copper catalyst also ensured efficient transformations, and the application of the *ortho*-bromophenyl derivative (**6m**) provided the highest yield (93%, entry 18) of the adduct. Finally, the *in situ* formation of a [Cu(NN)(MeCN)<sub>n</sub>]<sup>+</sup> species from Cu(MeCN)<sub>4</sub>PF<sub>6</sub> + 2.5 mol% **2m** resulted in only 41% yield of **9a** (entry 19). This result shows that the formation of a monoligated active species by dissociation of one of the diimine ligands during catalytic conditions is highly unlikely.

After finding the best catalyst system for the photocatalytic ATRA reaction of styrene and  $\text{CBr}_4$  we performed the addition reaction of various styrene derivatives in the presence of **6m** under the optimized reaction conditions (Scheme 2), and we obtained the appropriate tetrabromopropyl benzenes **9a–f** in moderate to excellent yields (54–93%). It is of note that we also tested different non-activated alkenes as substrate, but their transformation resulted lower conversion.<sup>16</sup>

We also studied the ATRA-type reaction of styrenes in which



**Scheme 3** Synthesis of iodides **11** and alkenes **12**.

iodine and  $\text{CF}_2\text{COOR}$  group could be installed onto the  $\text{C}=\text{C}$  double bond to access fluoroalkylated benzyl iodides as novel compounds, ready for further functionalization. We found that the addition reaction of  $\text{ICF}_2\text{COOEt}$  (**10**) and styrene took place in the presence of **6d** catalyst under the previously used reaction conditions, and **11a** was obtained in 75% yield (Scheme 3, Method A). Next, a series of iodo compounds **11** were prepared from substituted styrenes, and each target compounds could be obtained in good yields (75–83%) with the use of the new photocatalyst in 3-6 hours.

Although, iodides **11** could be synthesized, purified by chromatography, and characterized through the conventional manner, these compounds showed tendency to slow decomposition to alkenes **12** upon storage. This chemical behaviour could be controlled and the process could be accelerated by the addition of triethylamine as a base. Therefore, another series of reactions were



run in order to prepare alkenes **12** following Method B (Scheme 3). After irradiation for 3 hours, treatment of the reaction mixture with 3 equivalents of Et<sub>3</sub>N resulted in the formation of alkenes **12a–f** in 64–79% yield, depending on the type (Cl, F, Me) and position (*ortho*, *meta*, *para*) of the substituent on the aromatic ring of the styrene.

In conclusion, we designed and synthesized a series of inexpensive and readily available bis-imino copper(I)-complexes and studied their photocatalytic activity in different ATRA reactions. We found that the complexes could serve as good and economic alternatives to the existing copper based photocatalyst for the addition reaction of CBr<sub>4</sub> and ICF<sub>2</sub>COOEt to styrenes. We demonstrated that in the presence of copper complexes the photocatalytic transformations provide the appropriate adducts in good yield. Current work in our laboratory focuses on the application of this new photocatalyst family in various organic photoredox transformations.

The authors thank the support of the National Research, Development and Innovation Office (Grant No. NN118172), and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (Z.N.). The research was also supported by the EU and co-financed by the European Regional Development Fund under the projects GINOP-2.3.2-15-2016-00008, GINOP-2.3.3-15-2016-00004 and VEKOP-2.3.2-16-2017-00013 (K.Sz. and G.G.L.). This work was supported by the ELTE Institutional Excellence Program (1783-3/2018/FEKUTSRAT) and ÚNKP-17-1 (B. N.) New National Excellence Program of the Ministry of Human Capacities. This material is based upon work supported by the National Science Foundation under Grant No. 1358135 to T.J.P. There are no conflicts to declare.

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