

Organic & Biomolecular Chemistry

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Journal:	Organic & Biomolecular Chemistry		
Manuscript ID	OB-COM-06-2019-001331		
Article Type:	Communication		
Date Submitted by the Author:	11-Jun-2019		
Complete List of Authors:	Földesi, Tamás; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Adamik, Réka; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Sipos, Gellert; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Nagy, Bálint; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Tóth, Balázs; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Tóth, Balázs; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry Benyei, Attila; University of Debrecen, Department of Chemistry Szekeres, Krisztina; Eötvös Loránd University, Laboratory of Electrochemistry & Electroanalytical Chemistry Láng, Győző; Eötvös Loránd University, Laboratory of Electrochemistry & Electroanalytical Chemistry Demeter, Attila; Research Centre for Natural Sciences of the Hungarian Academy of Sciences Peelen, Timothy; Lebanon Valley College Novák, Zoltán; Eötvös Loránd University, ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry		

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Design and application of diimine-based copper(I) complexes in photoredox catalysis[†]

Tamás Földesi,^a Gellért Sipos,^{a, b} Réka Adamik,^a Bálint Nagy,^a Balázs L. Tóth,^a Attila Bényei,^c Krisztina J. Szekeres,^d Győző G. Láng,^d Attila Demeter,^e Timothy J. Peelen^{*f} and Zoltán Novák,^{*a}

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

www.rsc.org/

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.¹ 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.² 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.³ Bearing in mind the photochemical and redox properties there is opportunity to use cheaper transition metal complexes as sensitisers.⁴ In this respect, copper is a promising candidate, and several successful applications of copper complexes were already reported in different areas of photochemistry.⁵ Among the most active copper-based catalysts are phenanthroline complexes, such as homoleptic [Cu(dap)₂]Cl (1,⁶ Scheme 1), which shows impressive catalytic activity in photoredox transformations⁷ such as addition of CBr₄⁶ fluoroalkyl iodide,⁸ aryl- and alkylsulfonyl,9 and trifluoromethylsulfonyl chlorides10

^{b.} Current address: ComInnex Inc., Záhony u. 7, H-1031 Budapest (Hungary)

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to styrenes or alkenes, intramolecular cyclization and difluoromethylation of alkenes,¹¹ intermolecular cyclization of N-phenylmaleimide with *N*,*N*-dialkylaniline¹² or azidation reactions.¹³ It is worth mentioning that different heteroleptic copper complexes are also applicable as photocatalysts.¹⁴

Considering the structural features of these widely used excellent copper photocatalysts we aimed to design new bisimine type N,N donor ligands and study the photocatalytic activity of their copper complexes in atom transfer radical addition (ATRA) reactions.¹⁵ 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, Me₂N substituents in ortho, meta and para positions. For the synthesis of copper complexes, two equivalents of ligand 2 were used with Cu(MeCN)₄PF₆ 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.¹⁶ It is of note that, while some of these diimine ligands and their copper complexes have been reported previously¹⁷ to our best knowledge only few copper complex of this type has been applied in a photocatalytic synthesis.¹⁸

The main bands of the absorption spectra can be characterized with considerable large oscillator strengths (see Figure SI1), 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 CBr₄ a further kinetic increase of the TA signal may be observed at 460 nm

^{a.} ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry, Eötvös Loránd University, Institute of Chemistry, Pázmány Péter s. 1/A, H-1117 Budapest (Hungary) E-mail: <u>novakz@elte.hu</u>; web: zng.elte.hu

^{c.} University of Debrecen, Department of Physical Chemistry, H-4032 Hungary, Debrecen, Egyetem tér 1.

^{d.} Eötvös Loránd University Laboratory of Electrochemistry & Electroanalytical Chemistry, Eötvös Loránd University, Institute of Chemistry, Pázmány Péter stny. 1/A. H-1117 Budapest (Hunaary)

e. Research Centre for Natural Sciences of the Hungarian Academy of Sciences. H-1117 Hungary, Budapest, Magyar Tudósok körútja 2.

^{f.} Department of Chemistry, Lebanon Valley College, Annville, PA (USA) 17003. Email: peelen@lvc.edu

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

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Scheme 1 Design of new copper bis imine complexes.

Cyclic voltammogram of **6d** (1) 100 mM TBABF₄ in MeCN and (2) 1 mM $C_{36}H_{40}CuF_6N_4O_4P$ (**6d**) / 100 mM TBABF₄ in MeCN. v = 50 mV·s⁻¹; E = -1.73-0.77 V vs. SSCE. The working electrode was a GC (A = 0.031 cm²) plate.

with a characteristic time parameter of 100-200 μ 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 depositiondissolution 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.¹⁶

Complex 6m was also characterized by single-crystal X-ray crystallography (Scheme 1).¹⁹ The cation has C2 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 (N5-Cu1-N8 = 84.30° and N1-Cu1-N4 = 84.89°). Consequently, the interligand N-Cu-N angles are larger than those of a tetrahedral complex (N1-Cu1-N5 = 114.94°, N1-Cu1-N8 = 132.79°, N4-Cu1-N5 = 133.76°, and N4-Cu1-N8 = 113.29°, respectively). The angle of the CuN2 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 π - π stacking is unlikely as the two pairs of rings are substantially displaced laterally (average centroid distances are 5.2°).

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Table 1. Optimization of reaction conditions^a

+ CBr ₂ 7 8a	catalyst 520-525 nm LED DCM Ar, 20 °C	Br B	ir A A	r Ar CCu ⁺ , N PF ₆ - r Ar 6a-n
Entry	Catalyst	Ar (in 6)	Cat. mol%	yield (9a , %)
1	6a	C ₆ H₅	1.0	23
2	6a	C_6H_5	2.5	73
3	6a	C_6H_5	1.0	0ь
4	2a	C_6H_5	2.0	0 ^c
5	Cu(MeCN) ₄ PF ₆	-	3.0	0 ^d
6	6a	C_6H_5	1.0	0 ^e
7	6b	$4-Me_2N-C_6H_4$	2.5	8
8	6c	$4-MeO-C_6H_4$	2.5	53
9	6d	2-MeO-C ₆ H ₄	2.5	76
10	6e	2-Ph-C ₆ H ₄	2.5	88
11	6f	$4-CI-C_6H_4$	2.5	62
12	6g	$3-CI-C_6H_4$	2.5	79
13	6h	$2-CI-C_6H_4$	2.5	90
14	6i	2,4-Cl ₂ -C ₆ H ₃	2.5	83
15	6j	2,6-Cl ₂ -C ₆ H ₃	2.5	4
16	6k	$2-F-C_6H_4$	2.5	88
17	61	$4-Br-C_6H_4$	2.5	88
18	6m	$2-Br-C_6H_4$	2.5	93
19	Cu(MeCN) ₄ PF ₆ + 2.5 % 2m	-	2.5	41

 ^a reaction conditions: 1 equiv. CBr₄, catalyst, abs. DCM, argon atmosphere, rt, 18 hours, green LED. ^b in the dark (under Al foil). ^c only ligand 2a. ^d only Cu(MeCN)₄PF₆.
 ^e 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 CBr₄ (7) to styrene (8a) as the chosen model reaction (Table 1).^{5k, 6} 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)₂] 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 (NMe₂) 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).

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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.¹⁶ To probe the importance of steric effects over electronic ones we performed the reaction with 2,4-dichloro derivate 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)_n]⁺ species from Cu(MeCN)₄PF₆ + 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 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.¹⁶

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



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iodine and CF_2COOR group could be installed onto the C=C double bond to access fluoroalkylated benzyl iodides as novel compounds, ready for further functionalization. We found that the addition reaction of ICF₂COOEt (**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 Et₃N 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 serves as good and economic alternatives to the existing copper based photocatalyst for the addition reaction of CBr_4 and ICF_2COOEt 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.

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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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