

Schiff base Cu(I) catalyst for aerobic oxidation of primary alcohols

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ABSTRACT

We report here new copper(I)-Schiff base complexes for the selective oxidation of primary alcohols to aldehydes under ambient conditions (with 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), *N*-methylimidazole (NMI), ambient air, acetonitril and RT). Particularly, the copper(I) complex bearing *N*-(4-fluorophenyl)-1-(furan-2-yl)methanimine (**L2**) showed high activity in the series and gave near-quantitative yields in the oxidations of benzyl alcohol (99% yield in 1 h) and 1-octanol (96% yield in 24 h). Based on the X-ray structure determination, the complex has a square pyramidal coordination accomplished by two **L2** ligands and bromide as a counter anion. The oxidation reactions were monitored with UV–vis and *in situ* ATR-IR spectroscopy to study the changes in the catalytic structure and to elucidate the catalytic properties and the mechanistic details. Accordingly, detachment of one of the **L2** ligands from the complexes is related to the oxidation activity.

1. Introduction

Oxidation of alcohols to corresponding carbonyl compounds is one of the most important transformations in the chemical and the pharmaceutical industries. [1] The transformation is traditionally carried out with stoichiometric inorganic oxidants (e.g. CrO₃, MnO₂, hyper valent iodine) where the processes are costly and produce large amounts of hazardous waste. [2,3] To ease the environmental and economic burden related to the traditional oxidation reactions, catalytic methods that use ambient air, oxygen or H₂O₂ as a terminal oxidant have been investigated intensively during the last 20 years. [4–8]

Due to its common occurrence in the earth crust and the central role in various oxygenase enzymes, copper is an attractive catalytic metal for oxidation reactions. Particular effort has been addressed on the development of a catalyst system that mimics the function of galactose oxidase (GO) enzyme that selectively oxidizes primary alcohols to aldehydes in some species of fungi. [9–14] Similarly to the enzymatic mechanism, these man-made catalysts employ copper(II) as a catalytic center together with a radical tyrosyl/nitroxide ligand. [11] As an example, copper(II) complexes combined with a stable nitroxyl radical such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), molecular oxygen and K₂CO₃ enable the selectively aerobic oxidation of primary benzylic alcohols to their corresponding aldehydes in alkaline water solution. [15–17] Regardless the high activity towards benzylic alcohols, the challenge for the copper(II) based catalytic systems is the oxidation of aliphatic primary alcohols to their corresponding

aldehydes.

In this respect, copper(I) catalyst are interesting as they have shown high activity towards the oxidation of aliphatic primary alcohols. [18–22] Actively studied systems have been *in situ* prepared homogeneous catalysts, which are based on the combination of a copper(I) salts with coordinating additives such as TEMPO, *N*-methylimidazole (NMI) and bidentate ligands (e.g. 2,2'-bipyridine (bipy)). [19] Interestingly, these copper(I) systems enable the selective oxidation of unactivated and activated primary alcohols to aldehydes.

During recent years, studies related to copper-based catalytic systems have focused on the screening of different copper salts, bases and nitroxyl radicals. The alteration of the ligand away from bipy has attracted limited interest and reports are sparse. [23–26] In addition to the *in situ* preparation and the dynamic nature of the copper(I) catalytic systems, the exact structures and reaction pathways are hard to determine and thus the mechanistic understanding has remained as a challenge.

Herein, we report novel copper(I) catalysts based on Schiff base ligand systems for the selective oxidation of primary alcohols using mild conditions (ambient air as an oxidant, room temperature and TEMPO and NMI as additives). The copper(I) catalysts were synthesized with Schiff base ligands and **C2-Br** is fully characterized through single crystal XRD. Additionally, the structural changes around the copper(I) center were characterized and studied throughout the oxidation reaction with UV–vis and *in situ* IR.

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2. Experimental

Commercially available compounds were purchased and used without further purification unless otherwise stated. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer GC–MS analyses were performed on Agilent Technologies 7890B GC equipped with 5977B MSD, using an Agilent DB-WAX (30 m, 0.25 mm, 0.25 μm) column. The oxidation products were identified with GC–MS by comparison with commercial samples. The yield determinations were conducted with the GC–MS using calibration curves with acetophenone or 1,2-dichlorobenzene as an internal standard. The UV–vis absorption measurements were performed on a Hewlett Packard 8453 instrument using 1.0 cm plastic cuvettes at room temperature. For the *in situ* IR measurements a Mettler Toledo ReactIR™ 15 was used with a 6.3 mm AgX DiComp as the probe. The single-crystal X-ray diffraction study were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-K α radiation ($\alpha = 0.71073 \text{ \AA}$). ATR-IR spectra were measured with Bruker Alpha-p, with a diamond ATR-unit.

2.1. Ligand synthesis

The ligands (L1–L7) were prepared according to literature protocols [27]. Due to air sensitivity of the copper(I) complexes we carried out the reactions under argon. Furfural (1 eq.) and substituted anilines (1.1 eq.) were mixed in a 50 ml round bottom flask with dry MeOH (5 ml) and 3 \AA molecular sieves (MS). The reaction was stirred in RT for 1 h. The MS were filtered out and ^1H , ^{13}C NMR spectra were recorded from the crude oily product in CDCl_3 . L2: ^1H NMR (CDCl_3 , 500 MHz): δ 8.24 (s, 1H, N = CH), δ 7.67 (1 H, ar-H), δ 7.19 (2H, ar-H), δ 7.05 (2H, ar-H), δ 6.93 (1H, ar-H), δ 6.53 (1H, ar-H). All the ligands were synthesized accordingly.

2.2. Complex preparation

The new copper(I) complexes (C2–C7) bearing the *N*-(*X*)-1-(furan-2-yl)methanimine ligands (L2–L7) were synthesized by mixing the corresponding ligand and with a 5 ml MeOH suspension of Cu(I)Br/Cu(I)OTf (0.33 eq.) at room temperature stirred for 2 h and the prepared complexes were isolated by filtration. The precipitated complex was washed with 10 ml of cold MeOH and dried under vacuum. The complex was dried in vacuum and stored at $-84 \text{ }^\circ\text{C}$ under inert atmosphere. C2: IR assignment: 1611 nm^{-1} ($\nu = \text{C}=\text{N}$), 1502 nm^{-1} ($\nu = \text{furan}$), 1223 nm^{-1} ($\nu = \text{ArF}$), 1019 nm^{-1} ($\nu = \text{Ar}$), 842 nm^{-1} ($\nu = \text{furan}$), 753 nm^{-1} ($\nu = \text{sub. Ar}$), 519 nm^{-1} ($\nu = \text{furan}$). UV–vis: No Cu(II) signal at around 600–700 nm was visible. A broad signal at around 300 nm can be appointed to the ligand (aromatic groups). All other complexes were synthesized accordingly with the appropriate ligand and characterized with ATR-IR, UV–vis spectroscopy and Elemental Analysis (see ESI for more information).

2.3. Oxidations

A series of catalytic oxidation reactions was performed in 5 ml/3 ml MeCN solutions at room temperature under open air. The reaction was set up by adding 1 mmol of 1-octanol, 5 mol % of copper(I)catalyst, 5 mol % of TEMPO and 10 mol % of NMI into a 20 ml test tube, which was equipped with a magnetic stirrer bar. The reaction was stirred 1500 rpm for 24 h for 1-octanol, 3 h for cinnamyl alcohol and 3-phenyl-1-propanol and 1 h for benzyl alcohol. After the reaction, 0.7 ml of the reaction solution and an internal standard (acetophenone 40 μl or 1,2-dichlorobenzene 40 μl , more information see ESI) were diluted with EtOAc (100 ml). GC samples (1.5 ml) were prepared by filtrating the solution through a layer of silica gel (1 cm thick). The yields were determined using GC–MS with calibration curves.

2.4. Crystal structure determinations

The single-crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-K α radiation ($\alpha = 0.71073 \text{ \AA}$). Heavy Atom Methods (SHELXS-97) [28] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2) [29]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(O) free). Semi-empirical absorption corrections and extinction corrections were applied. In C2-Br there is a 1/4 water per asymmetric unit (calculated using SQUEEZE [30,31], and from free refinement of highest electron difference density as water). The hydrogen atoms could not be localized and are not included in the refinement (see cif-file for details). C8 is a redetermination of ALAFOK (CCDC-1403822) at 123 K, for more detailed information see ESI [32].

C2-Br: orange crystals, $\text{C}_{22}\text{H}_{16}\text{BrCuF}_2\text{N}_2\text{O}_2 \cdot \frac{1}{4} \text{H}_2\text{O}$, $M_r = 526.32$, crystal size $0.30 \times 0.12 \times 0.04 \text{ mm}$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.5965(5) \text{ \AA}$, $b = 13.2221(6) \text{ \AA}$, $c = 12.6993(5) \text{ \AA}$, $\beta = 101.498(1)^\circ$, $V = 2072.65(15) \text{ \AA}^3$, $Z = 4$, $\rho = 1.687 \text{ Mg/m}^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.022 \text{ mm}^{-1}$, $F(000) = 1050$, $2\theta_{\text{max}} = 55.0^\circ$, 36,381 reflections, of which 4765 were independent ($R_{\text{int}} = 0.053$), 276 parameters, $R_1 = 0.028$ (for 3944 $I > 2\sigma(I)$), $wR_2 = 0.060$ (all data), $S = 1.04$, largest diff. peak/hole = $0.348/-0.578 \text{ e \AA}^{-3}$.

CCDC 1865444 (C2-Br) and 1865445 (C8) 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.

3. Results and discussion

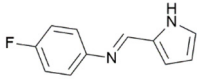
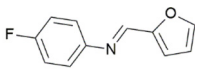
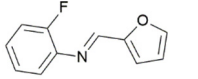
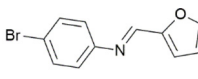
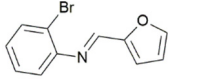
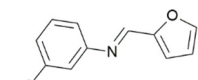
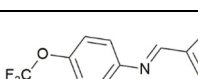
3.1. New catalysts

In the search of new homogenous catalyst systems, Schiff base ligands are particularly interesting, due to their straightforward modification. Furthermore, Schiff base ligands can give alternatives for bipy and porphyrin ligands, needed in the copper(I) oxidation catalysts. In this respect we examined our previous Schiff base ligands developed for a copper(II)-system [16], which were active for the oxidation of primary benzylic alcohols. From those we chose the most promising ligand (*N*-(4-fluorophenyl)-1-(pyroll-2-yl)methanimine (L1, $\text{C}_{11}\text{H}_9\text{FN}_2$) [33,34] for further studies with copper(I) catalysts.

To our surprise this copper(I) complex (C1 ($\text{C}_{11}\text{H}_8\text{FN}_2$) $_2\text{CuBr}$) with L1 showed no catalytic activity for the oxidation of 1-octanol to octanal under ambient conditions (Table 1, entry 1). We hypothesized that this was due to the different coordination mode between copper(I) and the bidentate ligand as in bipy and thus due to its inability to generate a catalytically active copper(I) center. This led us to the idea of introducing a five ring bearing oxygen as the second donor atom in the ligand. From the complex C2-Br (($\text{C}_{11}\text{H}_8\text{FNO}$) $_2\text{CuBr}$) crystals suitable for the single crystal X-ray measurement were obtained by slow evaporation of methanol. Since copper(I) is known to have commonly two-coordinate linear, three-coordinate trigonal planar or four-coordinate tetrahedral geometry [35], to find a stable Schiff base copper(I) complex with a square pyramidal coordination sphere (Fig. 1) is interesting. It is noteworthy that the bonds from furan oxygen donor to copper(I) are significantly longer than the bonds between copper(I) and imine nitrogen. We further expanded the series of complexes with furan based Schiff-base ligands having different substituted patterns on aniline (Table 1, C3–C7).

The impact these modified Schiff base ligands on the catalytic activity by oxidizing 1-octanol under ambient air was studied (Table 1). The highest yield for the oxidation of 1-octanol was obtained by using L2 ($\text{C}_{11}\text{H}_8\text{FNO}$) as a ligand forming isolated or *in situ* made complexes C2-Br (($\text{C}_{11}\text{H}_8\text{FNO}$) $_2\text{CuBr}$), Table 1, entry 2). Only modest reactivities were recorded with C3, C5, C6 and C7 bearing aniline with different

Table 1
Study of copper complexes with different ligand systems for the oxidation of 1-octanol.

$\text{C}_8\text{H}_{17}\text{OH} \xrightarrow[\text{MeCN, Ambient Air, RT, 24h}]{\text{Catalyst, TEMPO, NMI}} \text{C}_8\text{H}_{15}\text{CHO}$			
Entry	Catalyst ^d	Ligand	1-octanal Yield ^{b,c}
1	C1		no oxidation ^{c,d}
2	C2		80 % ^c 82 % ^d
3	C3		49 % ^d
4	C4		38 % ^d
5	C5		46 % ^d
6	C6		51 % ^d
7	C7		52 % ^d

^a Catalysts were prepared from Cu(I)Br salt (see ESI for details).

^b Oxidation conditions: 5 mol % TEMPO, 5 mol% catalyst, 10 mol % NMI, 1 mmol 1-octanol, RT, open air, 5 ml acetonitrile (MeCN), 24 h. Yield determination by GC–MS with internal standard (acetophenone).

^c *in situ* catalyst.

^d isolated catalyst.

^e CuBr alone gave 42% yield of 1-octanal.

substitution patterns (Table 1, entries 3 and 5–7). The lowest reactivity was observed with C4 (Table 1, entry 4). Although, low steric hindrance is important, these findings indicate that a substituent with a high electronegativity and para-directing properties is preferred at the aniline moiety of the ligand.

3.2. Catalytic reactions

The oxidation capability of C2 with bromide or triflate as an anion was further studied with different primary alcohols (Table 2). Changing the coordinated bromide anion to triflate had a marked influence to the catalytic reactivity in oxidation of 1-octanol and nearly quantitative yields were obtained (Table 2, entries 1, 2). This is a remarkable result as the reaction takes place in open air rather than under pure oxygen at room temperature. We further expanded the substrate scope with heptanol, citronellol, 3-(methylthio)-propanol, 3-phenyl-2-propyn-1-ol. They all were oxidized with good to excellent yields (Table 2, entries 13–20). In the case of allylic and benzylic primary alcohols, the

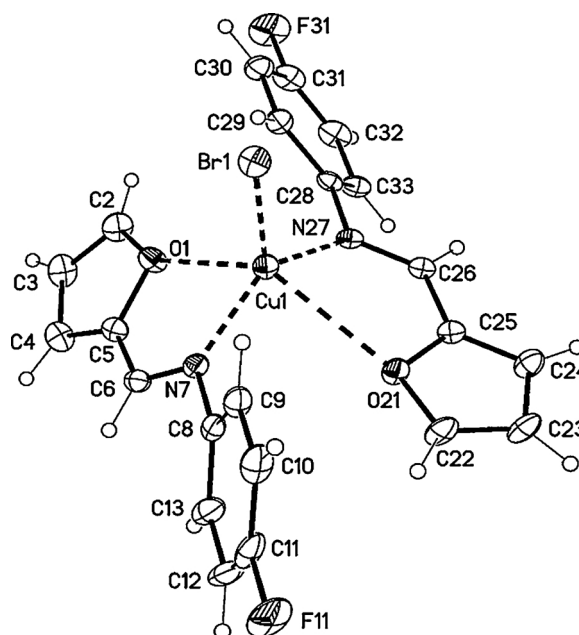


Fig. 1. A solid state structure of C2-Br (water omitted for clarity, displacement parameters drawn at 50% probability level). The crystal structure from C2-Br (Fig. 1) shows that the bonds between the furan oxygen donor and copper(I) (Cu1-O21 with 2.6998 Å and Cu1-O1 with 2.7192 Å) significantly longer are than the bonds between copper(I) and the imine nitrogen (Cu1-N7 with 1.9882 Å and Cu1-N27 with 2.0025 Å).



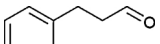
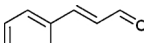
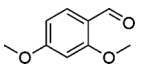
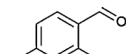
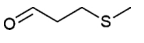
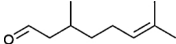
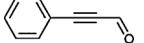

oxidation proceeds rapidly and quantitatively in 1–3 hours (Table 2, entries 3, 4, 7–12). No particular differences between bromide and triflate were observed in these oxidations. As an example of challenging alcohols, 3-phenyl propanol was oxidized in 3 h with 57% yield (Table 2, entry 6). Notably, elongated reaction time did not improve the reaction yields. Secondary alcohols, for example 2-octanol and diphenylcarbolol were hardly oxidized and as shown earlier by us, this is related to the steric bulkiness of TEMPO and can be overcome with a change of the NO-radical. [36] Importantly, GC–MS analytics showed that no over-oxidation to carboxylic acids occurred and no other side products were detected.

The oxidation pathways and reactions timescale of primary alcohols 1-octanol, benzyl alcohol were investigated for C2 with *in situ* IR (Fig. 2) and UV–vis. Accordingly, the oxidation of benzyl alcohol is completed in 1 h, while the oxidation of 1-octanol proceeds over the period of 24 h. This is a nice fingerprint of the stability of the catalytic system but does not explain why the reaction holds with 3-phenyl-1-propanol after 3 h (Table 2 entries 5 and 6). This is in a good accordance with GC–MS results.

Interestingly, according to *in situ* IR free Schiff base ligand appears, when the complex C2 in contact with the solvent (acetonitrile) and oxygen. This is clearly visible with the emerging signal at 1632 cm⁻¹ ($\nu_{\text{C=N}}$), which appears already after one minute (Fig. 3A). The detachment of the ligand does not occur without the presence of oxygen. Apparently, the ligand detachment opens the coordination sphere of the copper cation and generates possibilities to coordinate the reactants. This is most likely related to the formation of catalytic active species, as the aldehyde signal at 1725 cm⁻¹ appears alongside with the free ligand signal (for more details see ESI).

As shown above with the *in situ* IR measurements, the detachment of the ligand occurs only under aerobic conditions (Fig. 3). The reaction was further followed with UV–vis to detect possible changes in the oxidation state of copper(I)triflate complex. In the beginning of the reaction, the copper cation is in the oxidation state + I and in the UV–vis spectra a signal at 450 nm is detected. After the oxidation reaction only copper(II) species are present, which show as a broad and

Table 2
Oxidation of different primary alcohols.

$\text{R-CH}_2\text{-OH} \xrightarrow[\text{MeCN, Ambient Air, RT}]{\text{C2, TEMPO, NMI}} \text{R-CHO}$			
Entry	Catalyst ^d	Yield ^f (conversion)	Product
1	C2-Br ^b	82 % (82%)	
2	C2-OTf ^b	96 % (96%)	
3	C2-Br ^c	> 99 % (100%)	
4	C2-OTf ^c	> 99 % (100%)	
5	C2-Br ^d	41 % (41%)	
6	C2-OTf ^d	57 % (57%)	
7	C2-Br ^d	> 99 % (100%)	
8	C2-OTf ^d	> 99 % (100%)	
9	C2-Br ^d	> 99 % (100%)	
10	C2-OTf ^d	> 99 % (100%)	
11	C2-Br ^d	> 99 % (100%)	
12	C2-OTf ^d	> 99 % (100%)	
13	C2-Br ^e	78 % (78%)	
14	C2-OTf ^e	71 % (71%)	
15	C2-Br ^e	57 % (57%)	
16	C2-OTf ^e	93 % (93%)	
17	C2-Br ^e	> 99 % (100%)	
18	C2-OTf ^e	> 99 % (100%)	
19	C2-Br ^b	59 % (59%)	
20	C2-OTf ^b	94 % (94%)	

^a C2-Br = Catalyst with L2 and CuBr, C2-OTf = Catalyst with L2 and CuOTf. CuBr alone gave 42% yield of octanal and CuOTf gave 60% yield of octanal.

^b 5 mol % TEMPO, 5 mol % catalyst, 10 mol % NMI, 1 mmol alcohol, RT, open air, 3 ml Solvent, 24 h.

^c 5 mol % TEMPO, 5 mol % catalyst, 10 mol % NMI, 1 mmol alcohol, RT, open air, 5 ml Solvent, 1 h.

^d 5 mol % TEMPO, 5 mol % catalyst, 10 mol % NMI, 1 mmol alcohol, RT, open air, 5 ml Solvent, 3 h.

^e 5 mol % TEMPO, 5 mol % catalyst, 10 mol % NMI, 1 mmol alcohol, RT, open air, 5 ml Solvent, 24 h.

^f Yield: GC-MS: internal standard acetophenone for entries 1,2, 9–20 and 1,2-dichlorobenzene for entries 3–8.

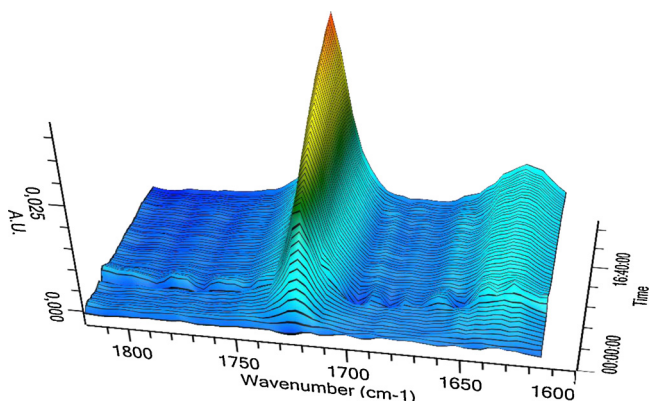


Fig. 2. *In situ* IR spectrum recorded during the oxidation of 1-octanol to 1-octanal with C2-OTf catalyst. The aldehyde peak appears at 1725 cm⁻¹ (more details ESI).

strong signal around 600–700 nm (see ESI for details). Under these conditions the oxidation of primary alcohols is bound to the copper(I)/copper(II) redox pair, as at the end of the oxidation reaction a strong copper(II) signal is present in each UV–vis spectrum. (See ESI). We

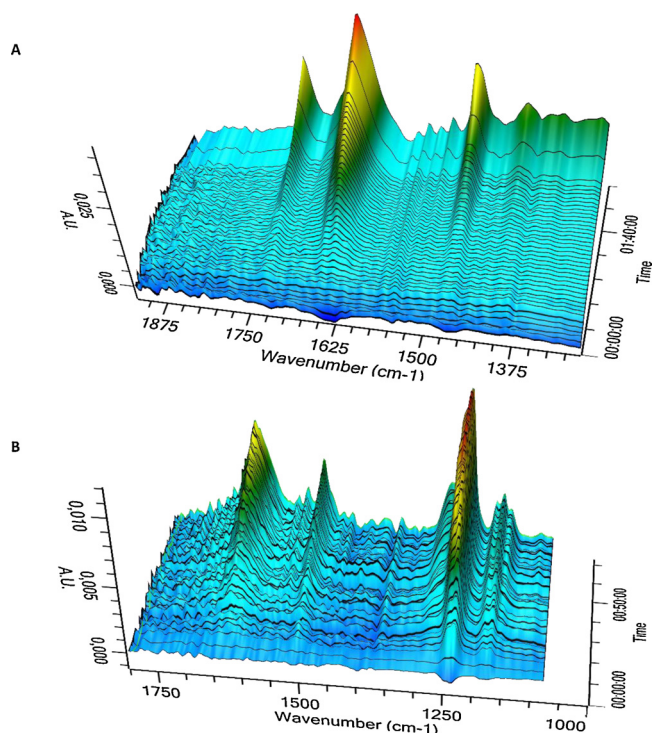


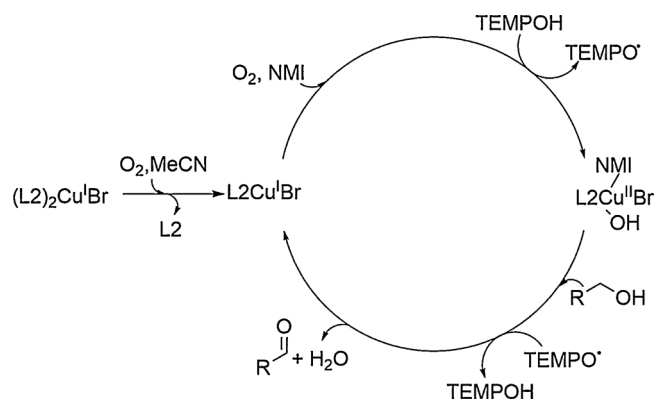
Fig. 3. A: *In situ* IR spectrum of the oxidation of 1-octanol with C2-Br catalyst. The main signal of the free ligand L2 at 1632 cm⁻¹ ($\nu_{\text{C=N}}$) and the signal belonging to 1-octanal at 1725 cm⁻¹ ($\nu_{\text{C=O}}$) are visible after the addition of oxygen to the reaction solution. B: IR spectra of C2-OTf complex in acetonitrile after adding oxygen. The signals of the detached L2 are as follows: $\nu_{\text{C=N}}$ at 1632 cm⁻¹, ν_{furan} at 1526 cm⁻¹ and $\nu_{\text{C-F}}$ at 1250 cm⁻¹.

propose the following reaction mechanism based on the UV–vis and *in situ* IR studies (Scheme 1).

It is particularly interesting to notice that the oxidation reaction does not take place without the presence of NMI as an additive. Under standard reaction condition the ligand detachment is evident but copper(II) signals are not visible in UV–vis spectra (see ESI). To study this further, we attempted to isolate the copper(II) complex from the reaction solution. With a marked excess of NMI, a second set of solid state crystals was obtained after the reaction. According to the solid state structure six NMIs are coordinated to the copper(II), giving a octahedral coordination sphere (see ESI for details on C8). [30] The loss of the second ligand is most likely causing the inactivation of the catalytic system, as copper(I) bromide and copper(I) chloride form similar NMI complexes over time and these themselves only give moderate reactivity in oxidation reactions.

4. Conclusion

As presented in this work, we have developed a new effective copper(I) catalysts for the selective aerobic oxidation of aliphatic, allylic and benzylic primary alcohols. The true novelty of the catalyst rises from the ligand framework, which is based on Schiff bases rather than on bipyridine. Due to the straightforward synthesis of Schiff bases, the ligand structure can be further modified. As shown here, the para 4-fluoro pattern on the aniline is important for receiving high reactivity and as a result quantitative oxidation of primary alcohols takes place under mild conditions, room temperature and open air. As the solid state structure shows a bisligand system, the *in situ* IR studies illustrates that the catalytic activity is linked to the ligand detachment under oxygen. This opens coordination sites for the substrate and additives to approach the copper center. Although the catalyst is rather stable over the long reaction time, the second ligand can also leave the



Scheme 1. The proposed reaction mechanism is based on previous studies [37,38] and the results of this work.

coordination sphere, which is most likely the deactivation pathway. Although the reported catalyst has noticeable catalytic activity in the series of reported copper(I) systems, further studies with modified Schiff base ligands related to Schiff base copper(I) complexes are ongoing.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.mcat.2019.02.003>.

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¹ The signal at 1526 cm⁻¹ is missing due to auto correction of the background.