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A new catalytic approach for aerobic oxidation of primary alcohols based on a Copper(I)-thiophene carbaldimines

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ABSTRACT

We report here novel Cu(I) thiophene carbaldimine catalysts for the selective aerobic oxidation of primary alcohols to their corresponding aldehydes and various diols to lactones or lactols. In the presence of the *in situ* generated Cu(I) species, a persistent radical (2,2,6,6-tetramethylpiperdine-N-oxyl (TEMPO)) and N-methylimidazole (NMI) as an auxiliary ligand, the reaction proceeds under aerobic conditions and at ambient temperature. Especially the catalytic system of *1-(thiophen-2-yl)-N-(4-(trifluoromethoxy)phenyl)methanimine* (ligand **L2**) with copper(I)-iodide showed high reactivity for all kind of alcohols (benzylic, allylic and aliphatic). In the case of benzyl alcohol even 2.5 mol% of copper loading gave quantitative yield. Beside high activity under aerobic conditions, the catalysts ability to oxidize 1,5-pentadiol to the corresponding lactol (86% in 4 h) and N-phenyldiethanolamine to the corresponding morpholine derivate lactol (86% in 24 h) is particularly noteworthy.

1. Introduction

One of the fundamental transformations in the chemical and pharmaceutical industry is the oxidation of alcohols to their corresponding aldehydes. [1–3] The reaction is required to be efficient, selective, fast and follow the principles of green chemistry. Classically, the method for this transformation is the use of stoichiometric inorganic oxidants (hyper valent iodine (Dess-martin reagents), Swern, CrO_3 or MnO_2). However, these reactions are costly, produce stoichiometric amounts of toxic waste, rely on harsh conditions and often show incompatibility with functional groups. [2,4–6] The main goal of the recent research in this field is to reduce the environmental burden. This can be achieved through the use of H_2O_2 or oxygen, but most preferably utilizing air under aerobic conditions as the oxidant in combination with a transition metal-based catalyst. [7–11]

In the last decade the research has focused on copper based catalysts, that are commonly bearing N-donor ligands like bipyridine or phenanthroline together with 2,2,6,6-tetramethylpiperdine-N-oxyl (TEMPO) a stable radical and N-methylimidazole (NMI) as an auxiliary base. This combination is known to generate a highly active catalytic species, which will selectively oxidize a wide range of primary alcohols to their corresponding aldehydes. [3,12–21] The current goal is to improve the catalytic activity and stability, to use ambient temperatures, pressure and air as an oxidant, while still achieving high functional group tolerance and high chemo selectivity. [22] For example, the copper(I) based catalysts are often highly sensitive to water, which is by definition the side-product in aerobic oxidation.

In this work we present new copper(I) catalysts bearing thiophene carbaldimine-type ligands. The benefit of the here reported copper(I) system is, that it can be prepared on the bench without any Schlenk or glovebox methods, while still providing quantitative yields of aldehyde under true aerobic conditions at room temperature.

2. Experimental

Commercially available compounds were purchased from Sigma-Aldrich except 4-fluoroaniline (from fluorochem) and benzyl alcohol (from abcr) and used without further purification unless otherwise stated. The ^{1}H, ^{13}C, HSQC and HMBC NMR spectra were recorded on a Bruker Avance NEO 400 MHz spectrometer. GC-FID analyses were performed on Agilent Technologies 7890B GC equipped with 5977B MSD, using an Agilent HP-Ms-5-UI (30 m, 0.25 mm, 0.25 μm) column or GC–MS with an Agilent Technologies 6890 N GC equipped with 5973 MSD, using an Agilent HP-Ms-5-UI (30 m, 0.25 mm, 0.25 μm) column. The oxidation products were identified via GC–MS by comparison with commercial samples. The yield determinations were conducted with the GC-FID using calibration curves with acetophenone or 1,2-dichlorobenzene as an internal standard. For the *in situ* IR measurements a Mettler

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Toledo ReactIR™ 15 was used with a 6.3 mm AgX DiComp as the probe.

2.1. Ligand synthesis

The ligands (**L1-L6**) were prepared according to literature protocol [23]. **L1**: 2-thiophenecarboxaldehyde (1 eq., 0.93 ml) and substituted anilines (1 eq., 0.95 ml) were mixed in a 50 ml round bottom flask with dry toluene (5 ml) and with two drops of formic acid. The reaction was stirred in RT for 2 h. The product was filtered and washed with dry n-hexane and dried under vacuum. ^{1}H and ^{13}C NMR spectra were recorded from the product in $CDCl_3$. **L1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H, *N*═CH), 7.54 (d, J = 5.0 Hz, 1H, ar-H), 7.50 (s, 1H, ar-H), 7.20 (m, 2H, ar-H), 7.16 (m, 1H, ar-H), 7.09 (d, J = 17.3 Hz, 2H, ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.35, 152.92, 147.57, 142.79, 132.39, 130.50, 127.90, 122.52, 115.98. All the ligands were synthesized accordingly (see ESI for details).

2.3. Oxidations

Oxidation reactions were performed in 3 ml or 5 ml MeCN solutions at room temperature under open air conditions. The reaction was set up by adding 4 mol% of copper(I)iodine, 4 mol% of ligand, solvent, 5 mol% of TEMPO, 1 mmol of alcohol and 10 mol% of NMI into a 20 ml test tube, which was equipped with a magnetic stir bar. The reaction was stirred at 1500 rpm for 1 h, 3 h or 24 h depending on the substrate.

After the reaction, the reaction solution and an internal standard (acetophenone 40 μL or 1,2-dichlorobenzene 40 μL, see ESI for more information) were diluted with EtOAc (50 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-FID with calibration curves and identified using GC–MS and/or ^{1}H/^{13}C/HMBC/HSQC NMR.

3. Results and discussion

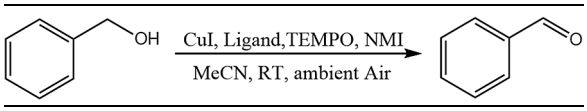
Our previous work showed that bidentate Schiff base ligands combining both an imine and a furan functionality, for example N-(4-fluorophenyl)−1-(furan-2-yl)methanimine, coordinate strongly with various copper(I) salts and generate in the presence of TEMPO and NMI highly reactive catalysts for the oxidation of primary alcohols. [14] Here we were interested to see how changes in this ligand structure would further improve the catalytic properties. In this regard, we were looking for ways to improve coordination stability of the heterocyclic part of the ligand and straightforward the exchange of furan to thiophene substitution was an appealing strategy. We synthesized six thiophene carbaldimines to be studied as supporting ligands in copper(I) based catalysts. The structure of the ligands and the synthetic pathways are shown in Fig 1.

The ligands **L1-L6** together with copper(I)-iodide as the copper source were introduced to the oxidation reaction using benzyl alcohol as a model substrate. In comparison with previous, furan based catalytic systems, this new Schiff base ligand copper system gave surprisingly high yields, when prepared *in situ* (in a 1:1 ratio of copper(I)-iodide to the ligand) (Table 1, entries 2, 7, 10, 11). In the series of thiophene carbaldimine ligands, **L2** gave the highest activity for benzyl aldehyde (Table 1, entries 1–6). When considering the catalytic activity in the ligand series, increasing the electronegativity of the para-substituent increases the catalytic activity. To rationalize these results, we should see the thiophene carbaldimines as bidentating ligands with a strongly coordinating thiophene functionality and with a weakly coordinating imine functionality. Thiophene coordination will keep the ligand attached to the copper(I), while the coordination strength of imine can be controlled by the para substituents; the higher the electronegativity of the substituent, the weaker the imine coordination and the higher the activity. This indicates the importance of hemilabile coordination around the copper(I) center. The dynamic coordination sphere provides the needed flexibility in the coordination sphere for the substrate coordination.

Under optimized conditions (5 mol% TEMPO, 4 mol% CuI, 4 mol% ligand, 10 mol% NMI, 1 mmol alcohol), it was possible to reduce the catalytic loading of **L2**CuI to 4 mol%, while still achieving high to quantitative yields (Table 1, entry 7, Table 2 entry 2). Furthermore, in the case of benzyl alcohol oxidation the catalytic loading could be reduced down to 2.5 mol% for the **L2**CuI catalyst (Table 1, entry 8). [14, 24,25] However, a longer reaction time of 3 h was needed to achieve quantitative yields.

To demonstrate the high reactivity of this new copper(I) catalyst, the oxidation of various primary alcohols were studied under optimized conditions (4 mol% CuI, 4 mol% ligand, 5 mol% TEMPO, 10 mol% NMI, 1 mmol alcohol). All π-activated substrates (such as cinnamyl alcohol, 3-phenyl-2-propyn-1-ol, 2,4-dichlorobenz alcohol, 2,4-dimetoxybenzyl alcohol, 4-methoxybenzyl alcohol, 4-nitrobenzyl alcohol, methyl 4-

Table 1
Aerobic oxidation of benzyl alcohol.



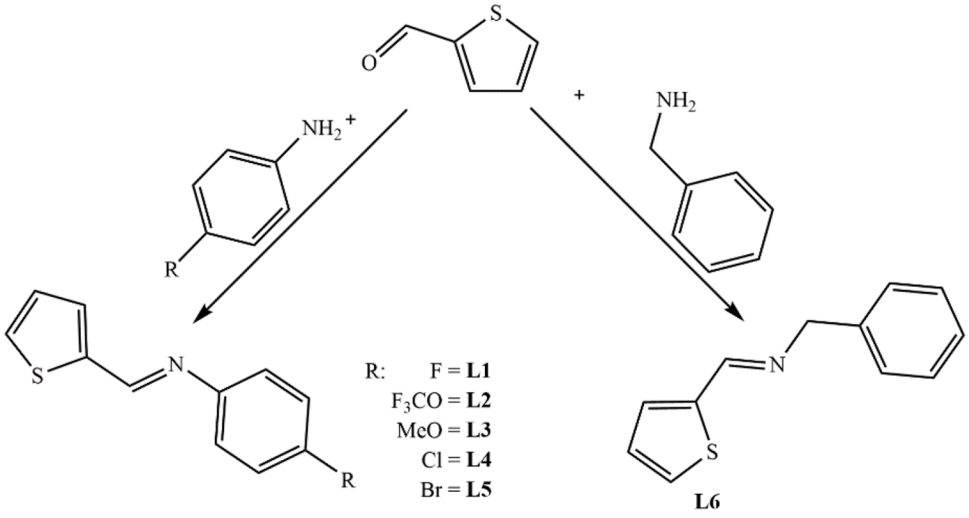
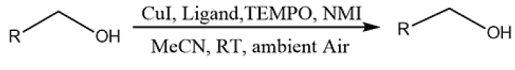
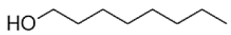
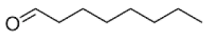
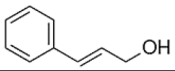
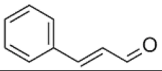
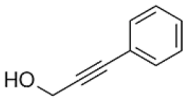
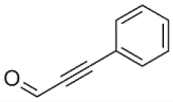
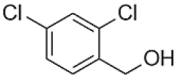
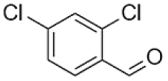
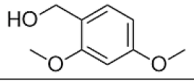
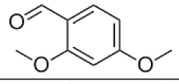
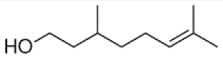
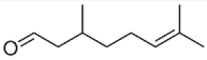
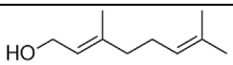
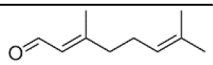
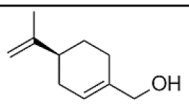
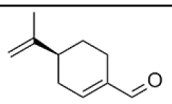
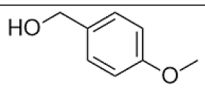
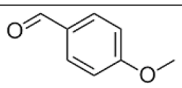
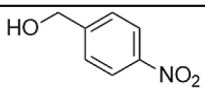
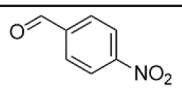
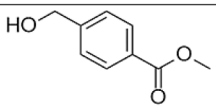
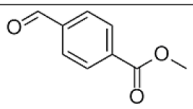
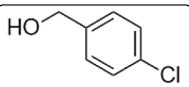
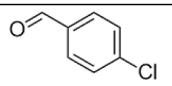


Fig 1. Schematic pathway of the synthesis for the different ligands **L1-L6** prepared for this work.

Table 2
Aerobic oxidation of different primary alcohols.

Table 2. Aerobic oxidation of different primary alcohols



Entry	Catalyst	Yield[e] (conversion)	Starting material	Product
1 2	CuI with **L1** CuI with **L2**	**67% (67%)[a]** **75% (75%)[a]**		
3	CuI with **L2**	**>99% (100%)[a]**		
4	CuI with **L2**	**98% (99%)[a]**		
5	CuI with **L2**	**>99% (100%)[b]**		
6	CuI with **L2**	**>99% (100%)[b]**		
7	CuI with **L2**	**91% (92%)[c]**		
8	CuI with **L2**	**98% (100%)[a] (E:Z 98:2)[d]**		
9	CuI with **L2**	**>99% (100%)[b]**		
10	CuI with **L2**	**>99% (100%)[b]**		
11	CuI with **L2**	**>99% (100%)[b]**		
12	CuI with **L2**	**>99% (100%)[b]**		
13	CuI with **L2**	**>99% (100%)[a]**		

[a] 5 mol % TEMPO, 4 mol % CuI, 4 mol % ligand, 10 mol % NMI, 1 mmol alcohol, RT, open air, 3 ml Solvent, 24 h.
[b] 5 mol % TEMPO, 4 mol % CuI, 4 mol % ligand, 10 mol % NMI, 1 mmol alcohol, RT, open air, 3 ml Solvent, 3 h.
[c] 5 mol % TEMPO, 4 mol % CuI, 4 mol % ligand, 10 mol % NMI, 1 mmol alcohol, RT, air balloon, 3 ml Solvent, 24 h.
[d] Characterized with ^{1}H, ^{13}C, HMBC and HSQC NMR (see ESI for more information)
[e] Yield calculated with GC-FID calibration curves (see ESI for more information)

(hydroxymethyl)benzoate and 4-chlorobenzyl alcohol) gave quantitative yields of the corresponding aldehyde with the use of 4 mol% loading of the **L2**CuI catalyst (see Table 2, entries 3–6, 10–13). Using 1-octanol as an example of aliphatic primary alcohols gave 75% yield and citronellol gave 91% yield for the corresponding aldehyde (see Table 2, entries 2, 7).

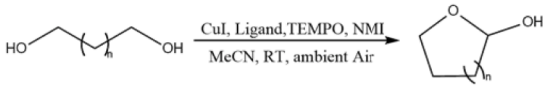
To our surprise the quantitative oxidation of geraniol resulted in only the E-isomer of citral (Table 2, entry 8). This was confirmed through ^{1}H, ^{13}C, HMBC and HSQC NMR measurements (see ESI). In addition, the oxidation of (*S*)-(−)-perillyl alcohol gave a quantitative yield of the corresponding aldehyde (Table 2, entry 9), without overoxidized side products.

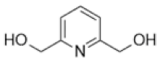
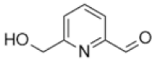
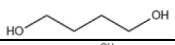
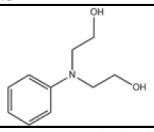
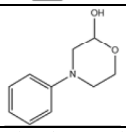
To broaden our substrate scope, we focused also on the oxidation of various diols. In general, diols are interesting substrates, due to their corresponding heterocyclic oxidation products. Oxidation of aliphatic primary diols with the use of a well-studied bipyridine-copper system has been reported to proceed through a lactol-intermediate giving lactones at a very high yield. [26] Similarly, a enzymatic pathway is reported to be selective towards lactones. [27,28] Unexpectedly, our copper(I)-thiophene carbaldimines system has a distinct selectivity. We were able to obtain corresponding lactols as the main product rather than the expected lactones (Table 3, entries 1 and 4).

The lactol structure was confirmed with ^{1}H, ^{13}C, HMBC and HSQC NMR of the reaction mixture (see ESI). Experiments with *in situ* IR confirmed that the lactol forming cyclisation reaction was immediate, since there is no aldehyde signal detectable while following the reaction

Table 3
Aerobic oxidation of different primary diols.

Table 3. Aerobic oxidation of different primary diols



Entry	Conversion to product[c] (total conversion)	Starting material	Product
1	86% (91%) [a]		
2	95% (99%) [a]		
3	95% (95 %) [b]		
4	86% (96 %) [b]		

[a] 5 mol % TEMPO, 4 mol % CuI, 4 mol % ligand **L2**, 10 mol % NMI, 1 mmol alcohol, RT, open air, 3 ml Solvent, 4 h.
[b] 5 mol % TEMPO, 4 mol % CuI, 4 mol % ligand **L2**, 10 mol % NMI, 1 mmol alcohol, RT, open air, 3 ml Solvent, 24 h.
[c] Conversion calculated with GC-MS through comparison of integrals and structure identified with ^{1}H, ^{13}C, HMBC and HSQC NMR (see ESI for more information)

over time (Fig 2B). The evolving signal of benzyl aldehyde in Fig 2A at 1704 cm^{-1} is a typical example of a oxidation reaction, where the reaction proceeds quickly, aldehyde product accumulates and becomes the dominant signal in the *in situ* IR spectra.

When following the aerobic oxidation, the lack of aldehyde signal in the *in situ* IR (Fig 2B) spectra is striking and explains why a lactol is obtained as the main product instead of the lactone. Our copper(I) system is selective towards the oxidation of primary alcohols to aldehydes and when the lactol forms in the cyclisation reaction, one of its hydroxyl groups changes into secondary alcohol, which is not further oxidized under these conditions even by longer reaction times (see ESI Table S3). The catalytic approach for the aerobic oxidation of N-phenyldiethanolamine to its lactol is a novel and straightforward synthesis of a valuable morpholine derivate (4-phenylmorpholin-2-ol) (Table 3, entry 4). [29,30] However, with 1,4-butandiol, the lactone is in the most thermodynamically stable form and is observed in very high yields (Table 3, entry 3). The oxidation of 2,6-pyridinedimethanol astonished us, since we were able to selectively oxidize only one of the two primary alcohols to aldehyde (Table 3, entry 2). The lactol structures were all confirmed with ^{1}H, ^{13}C, HMBC and HSQC NMR (see ESI).

Conclusion

In conclusion we have developed a new highly efficient copper(I) catalyst for the selective aerobic oxidation of aliphatic, allylic and benzylic primary alcohols to their corresponding aldehydes in high yields. Also, the system affords the selective oxidation of diols to primarily lactols. The novelty of this system lies in the bench stability of the new thiophene carbaldimine-copper(I)-iodide catalyst and in the lower catalytic loading of the system combined with the high reactivity in aerobic conditions. Due to its Schiff base character the ligand system is easy to synthesize and modify. However, electron withdrawing substitution at the para position of the aniline is deemed necessary for the high reactivity with CuI. In general, this work together with our previous work underlines the key role of the ligand for the further development of novel copper(I) base catalysts for the aerobic oxidation of alcohols. Further studies on CuI catalysts are ongoing.

CRediT authorship contribution statement

Emi Lagerspets: Conceptualization, Data curtion, Investigation, Writing – original draft, Writing – review & editing. **Evelyn Valbonetti:**

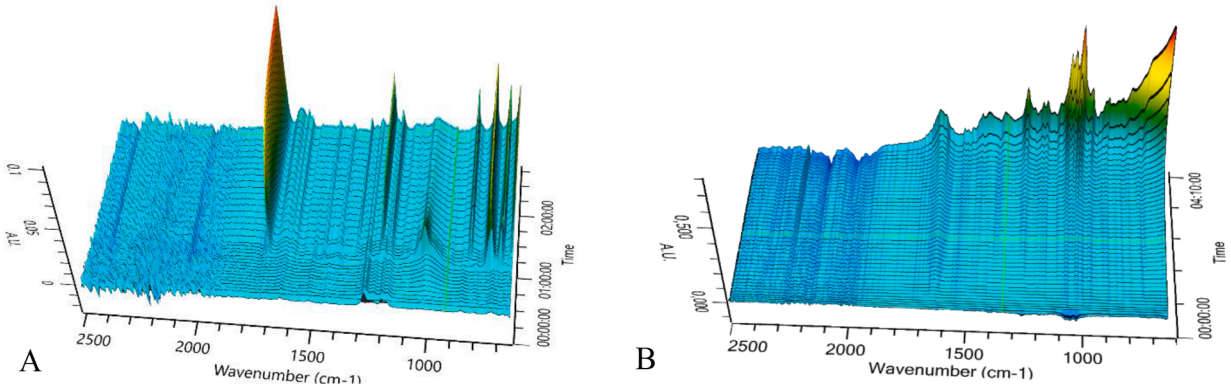


Fig 2. A) *In situ* IR spectra of the aerobic oxidation of benzyl alcohol with the L2CuI catalyst for 1 h. B) *In situ* IR spectra of the aerobic oxidation of 1,5-pentadiol with the L2CuI catalyst for 4 h.

Investigation. **Aleksi Eronen:** Investigation, Writing – review & editing. **Timo Repo:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2021.111637.

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