DOI: 10.1002/adsc.200900478

Aerobic Oxidation of Benzylic Alcohols in Water by 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)/Copper(II) 2-*N*-Arylpyrrolecarbaldimino Complexes

Paweł J. Figiel,[a,b] Ahlam Sibaouih,[a] Jahir Uddin Ahmad,[a] Martin Nieger,[a]
Minna T. Räisänen,[a,c] Markku Leskelä,[a] and Timo Repo[a,*]

[a] Laboratory of Inorganic Chemistry, Department of Chemistry, P. O. Box 55, FI-00014 University of Helsinki, Finland
Fax: (+358)-9191-50198; phone: (+358)-9191-50194; e-mail: timo.repo@helsinki.fi
[b] Current address:Centro de Quimica Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[c] Current address: School of Chemistry, University of St. Andrews, North Haugh, St. Andrews KY16 9ST, United Kingdom

Received: July 9, 2009; Published online: October 28, 2009

Supporting information for this article is available on the WWW under
http://dx.doi.org/10.1002/adsc.200900478.

Abstract: Novel copper(II) 2-*N*-arylpyrrolecarbaldimine-based catalysts for the aerobic oxidation of benzylic alcohols mediated by the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical are reported. The catalytic activity for both synthesized and *in situ* made complexes in alkaline water solutions was studied revealing high efficiency and selectivity (according to GC selectivity always >99%) for both of these catalytic systems. For example, quantitative conversion of benzyl alcohol to benzaldehyde can be achieved with the *in situ* prepared bis[2-*N*-(4-fluorophenyl)-pyrrolylcarbaldimide]copper(II) catalysts in 2 h with atmospheric pressure of O_2 at 80 °C. Interestingly, these catalysts can utilize dioxygen as well as air or hydrogen peroxide as the end oxidants, producing water as the only by-product.

Keywords: aerobic oxidation; catalysis; copper; dioxygen; green chemistry; 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)

Introduction

The choice of an appropriate solvent as a reaction medium is gathering increasing attention in modern synthetic chemistry, not only in terms of reactivity and selectivity but also sustainability.[1] Particularly, the use of non-toxic and halogen-free solvents is one of the major principles of green chemistry.[2] In this respect water, being safe and the most accessible solvent, is an attractive medium for chemical transformations. However, its use is still rather uncommon in catalytic reactions, not only because of the limited solubility of reagents, but also because of the water-sensitivity of the catalytic active species.[1,3]

Oxidation of alcohols to their corresponding carbonyl products is one of the fundamental transformations in organic chemistry;[4] benzylic aldehydes, for example, are versatile intermediates for perfumery and other syntheses of fine chemicals.[5] In large-scale applications the replacement of classical methodologies, based on stoichiometric oxidants such as chromates, selenium dioxide or manganese dioxide, by green sources of oxygen (dioxygen, air, H_2O_2) is highly desirable.[6] The price, atomic efficiency and non-toxic by-products of these end oxidants make them attractive candidates for sustainable alcohol oxidation.[7] As water is usually the main by-product in the oxidation reactions with dioxygen or air, catalytic systems requiring anhydrous conditions are inherently impractical.[4]

Palladium diimine complexes were recently reported as active catalysts in the oxidation of alcohols in water using air or dioxygen as the end oxidant.[4,8] However, replacement of relatively rare, precious elements (Pd, Pt, Ru) with more abundant and cheaper metals (Fe, Cu) could offer a substantial cost saving.[9] In this respect, the recent results with Cu-based, water-tolerant catalysts are attractive. Copper(II) diimine complexes when combined with TEMPO as a mediator have shown great efficiency in oxidation reactions.[10,11] As recently published by Sheldon et al.[11] and Reedijk et al.[12], TEMPO/Cu-bipyridine and TEMPO/Cu-pyrazole systems oxidize benzyl alcohol at room temperature and under atmospheric air.

However, these systems require moderately high catalyst loadings (5 mol%), addition of a co-solvent (2:1 acetonitrile:water) and an activator (*t*-BuOK). Interestingly, as we have shown previously, TEMPO/Cu-diimine catalysts can also provide efficient oxidation in pure aqueous alkaline solutions; however this requires increased temperature and oxygen pressure.[13] As a result of our current investigations, we report herein a novel, markedly improved and highly active catalytic system based on copper 2-*N*-arylpyrrolecarbaldimino complexes for aerobic oxidation of benzylic alcohols in alkaline water solutions.

Results and Discussion

While looking for new bidendate, nitrogen-based ligand candidates to substitute classical bipyridine and phenanthroline in catalytic systems and to further improve catalytic activity, our attention was focused on 2-pyrrolecarbaldimine ligands. These ligands are interesting intermediates between bipyridines and phenoxyimines, the latter being a substructure of classical salen-type ligands. Although transition metal complexes of these monoanionic ligands have been known since the 1920s[14] and these chelates share common features with porphyrins, their catalytic properties have not been extensively studied. Recently 2-pyrrolecarbaldimine-based titanium catalysts were reported for olefin polymerization,[15] while Cu(II) complexes bearing 2-pyrrolecarbaldimine ligands have been used as precursors in ALD applications for the growth of Cu(0) surfaces.[16]

For this study a series of 2-*N*-arylpyrrolecarbaldimine ligands and their corresponding Cu(II) complexes were selected in order to investigate their catalytic properties in the oxidation of benzylic alcohols in alkaline water (Figure 1). Interestingly, the ligands and the complexes can be formed by a simple condensation reaction between pyrrole-2-carbaldehyde and the appropriate aniline derivative in the presence of a selected transition metal salt in a one-pot synthesis.[17] This reaction can even be carried out in water, which underlines the inherent stability of the Cu(II) complexes.[18] Ligands with different substitutents were selected, according to their electron-withdrawing and electron-donating properties, including complex **5** possessing bulky steric groups in the vicinity of the imine nitrogen. Crystals of complexes suitable for single crystal X-ray measurements were obtained by recrystallizing the complexes from appropriate solvents (see Supporting Information).

Catalytic Oxidation

The oxidation of benzyl alcohol was chosen as a model reaction to study the oxidation potential of the Cu(II) 2-*N*-arylpyrrolecarbaldimino complexes in alkaline water solutions using O_2 as the end oxidant (Figure 2). As previously reported, the efficient oxidation reaction catalyzed by Cu(II) diimine complexes requires highly alkaline reaction conditions (NaOH, pH > 12.6).[13,19]

In the case of **1–5**, both NaOH and K_2CO_3 have an equally beneficial influence on the catalytic activity. This is one of the marked differences to the previous Cu(II) diimine catalysts. For further studies K_2CO_3 was selected, as the overall pH of the reaction mixture remains moderate, being now between 11 and 11.5. Although the 2-*N*-arylpyrrolecarbaldimino com-

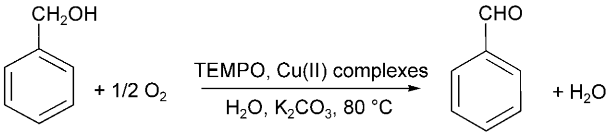


Figure 2. Model reaction for copper(II) 2-*N*-arylpyrrolecarbaldimine-based oxidation systems.

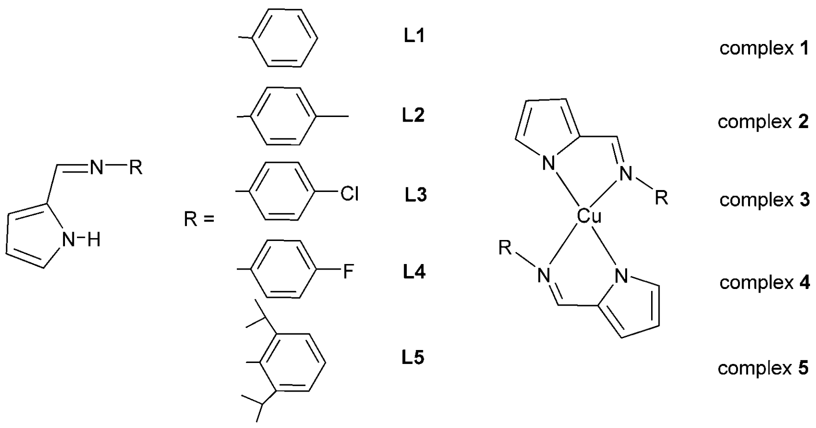


Figure 1. Schematic structures of ligands and their corresponding $Cu(L)_2$ complexes used in the study.

Table 1. Oxidation of benzyl alcohol in alkaline water, catalyzed by *in situ* and pre-made copper(II) 2-*N*-arylpyrrolecarbaldimino complexes.[a]

Run	Catalytic system	Conv.[b] [%]	Total O_2 uptake[c] [mmol]	V_{max}[c] [mmol O_2/min]
1	Complex **1**	45	0.66	0.0186
2	Complex **2**	74	0.91	0.0178
3	Complex **3**	95	1.12	0.0210
4	Complex **4**	99	1.20	0.0387
5	Complex **5**	6	0.13	0.0026
6	$CuSO_4$+**L1** (1:2)	91	0.95	0.0182
7	$CuSO_4$+**L2** (1:2)	89	0.96	0.0197
8	$CuSO_4$+**L3** (1:2)	94	1.08	0.0241
9	$CuSO_4$+**L4** (1:2)	100	1.17	0.0297
10	$CuSO_4$+**L5** (1:2)	3	0.05	0.0003
11[d]	$CuSO_4$+**L1** (1:2)	2	0.08	0.0005
12	$CuSO_4$	<1	0.02	0.0004

[a] *Reaction conditions:* see Figure 3 and Figure 4.

[b] Conversions of benzyl alcohol were measured by GC using internal standards, selectivity of benzaldehyde always >99% according to GC-MS.

[c] Maximum rate of dioxygen uptake, calculated from the slopes in Figure 3 and Figure 4.

[d] Reaction without TEMPO.

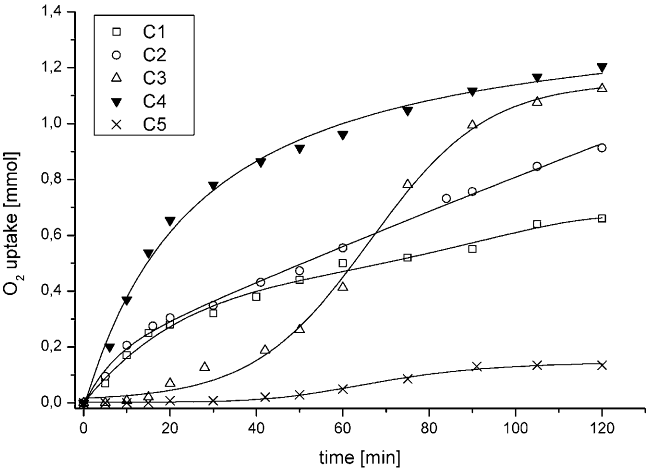


Figure 3. The activity of complexes **1**–**5** in the aerobic oxidation of benzyl alcohol. *Reaction conditions:* 3 mmol of benzyl alcohol, 0.15 mmol of TEMPO, 0.03 mmol of $Cu(L)_2$, 80 °C, 1 atm O_2, 2 h, 0.1 M K_2CO_3. Conversion values at the end points are given in Table 1.

plexes have similar activity to the previously reported phenanthroline-based catalysts at elevated temperature (80 °C) and dioxygen pressure (10 bar), they turned out to have also marked catalytic activity under atmospheric O_2 pressure. In the oxidations presented here, the presence of TEMPO and elevated temperature appeared to be essential for high conversions of the substrate (Table 1).

Comparison of the Catalysts

The oxidation reaction with copper(II) 2-*N*-arylpyrrolecarbaldimino complexes **1**–**5** as catalyst precursors was simultaneously followed by GC and dioxygen uptake measurements. When put together these data facilitate an insight to the catalytic oxidation (Figure 3). The oxidation reaction catalyzed by phenyl-substituted complex **1** proceeds with moderate efficiency (conversion 45%), while the presence of the *p*-methyl substitutent activates the catalyst and conversion rises to 74% (Table 1, complex **2**). According to dioxygen uptake measurements with both catalysts, the oxidation starts instantly and proceeds after first 10 min rather linearly.

Although *p*-Cl-substituted **3** gives very high conversions under the same reaction conditions (95%), the oxygen uptake measurements shows a relatively long induction time (20 min), after which a rapid reaction takes place. Complex **4** bearing the *p*-F substitutent, has the opposite behaviour to **3**. The beginning of the oxidation reaction with **4** is very fast giving the highest V_{max} rate (0.0387 mmol O_2/min) in the series. During the first 20 min around half of the substrate is already consumed. However, the rate gradually decreases with time and after the 2 h reaction the conversions with **3** and **4** are practically the same (Table 1). With regard to the catalytic activity, the ligand substitutents in the phenyl ring seem to have a substantial influence. Complex **5** with the bulky 2,6-diisopropyl-substituted ligand is barely reactive (Figure 3). Presumably, this is due to steric interactions caused by the ligand around the catalytically active copper(II) center (see Supporting Information).

One of the intriguing properties of the previously reported Cu(II) diimine catalysts is that they can be prepared *in situ* in alkaline solutions. This noticeably simplifies the catalyst preparation.[13,19] Encouraged by the previously published one-pot synthesis of similar compounds in alkaline water,[18] the possibility to apply *in situ* catalyst preparation was studied. By simple mixing of appropriate amounts of the reagents, $CuSO_4$, 2-*N*-arylpyrrolecarbaldimine ligand **4**, K_2CO_3 and TEMPO, a green, slightly disturbed homogeneous solution is formed. In this step the presence of K_2CO_3 facilitates the deprotonation and therefore better dissolution of the ligand.

After *ca.* 30 min of stirring at 80 °C, a brown precipitate appears, which is based on the analysis the desirable Cu(II) complex. The copper concentration of the solution was followed by atom absorption spectrophotometry (AAS) measurements and after complexation [Cu] decreases to 1.4 mg/dm^3 from the initial value of 218 mg/dm^3. In order to prove that the remaining [Cu] is due to the actual complex and not from un-

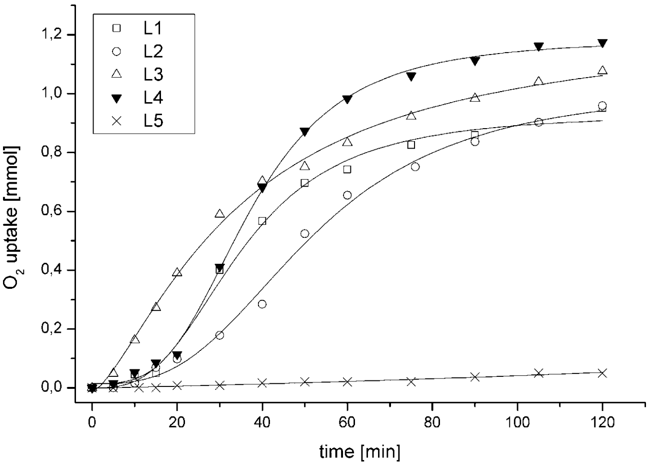


Figure 4. The activity of *in situ* prepared Cu(II) 2-*N*-arylpyrrolecarbaldimino complexes in the aerobic oxidation of benzyl alcohol. *Reaction conditions:* 3 mmol of benzyl alcohol, 0.15 mmol of TEMPO, 0.03 mmol of $CuSO_4$, 0.06 mmol of appropriate ligand, 0.1 M K_2CO_3, 80 °C, 1 atm O_2, 2 h.

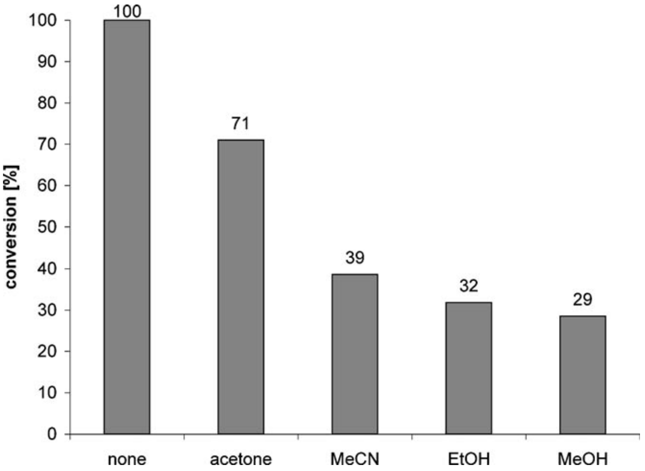


Figure 5. The effect of cosolvent on the conversion of benzyl alcohol. *Reaction conditions:* $CuSO_4$ (1 mol%), **L4** (2 mol%), H_2O/cosolvent = 95/5 v/v, otherwise same as in Figure 4.

reacted $CuSO_4$, a reference sample was prepared from the crystalline pre-made complex **4**. In both cases [Cu] in water were similar (1.8 mg/dm^3 in the case of pre-made complex), proving that this value reflects the actual complex concentration in the solution. When benzyl alcohol is added to start the oxidation, the [Cu] in the solution slightly increases (up to 2.2 mg/dm^3). In the end of the oxidation reaction a separate organic phase containing aldehyde and alcohol is observed and the [Cu] of the water phase is ~30 mg/dm^3. It is worthy of note that $CuSO_4$ alone has no catalytic activity (Table 1, run 12).

The *in situ* prepared Cu(II) 2-*N*-arylpyrrolecarbaldimino complexes provide highly efficient oxidation reactions, comparable to those catalyzed by the above described pre-made complexes (Table 1). The most important difference between the catalytic systems based on the *in situ* made and the pre-made complexes is in the reaction kinetics (Figure 4). All *in situ* catalysts are rapidly activated and reactions proceed with fairly similar rates, the halogenated ones remaining slightly more active. As in the case of the pre-made complexes, *in situ* made **5** possesses very low activity. Interestingly, all pre-made and *in situ* systems are highly selective (>99%) according to GC-MS analyses. The optimal ligand to metal ratio for the *in situ* catalyst was 2:1 (see Supporting Information).

Variation of Reaction Conditions

The Effect of Cosolvent

The most active *in situ* made catalyst combination ($CuSO_4$/**L4**) was selected for further studies (Figure 5). In order to explore whether better dissolution of catalyst would improve catalytic activity, different solvent pairs were studied. Although the addition of cosolvent (MeCN, EtOH, MeOH or acetone) improves dissolution and more homogeneous catalyst solutions were obtained,[12] even small amounts of cosolvents deactivate the present catalytic system. It is likely that the cosolvents compete with the substrate and/or O_2 for coordination to the catalytic active copper center.

The Effect of the Catalyst to Substrate Ratio

As shown in Table 2 (run 1), with a catalyst to alcohol ratio of 1:100 almost quantitative conversions were achieved. As shown in Figure 6, by increasing the ratio to 1:200 similar conversions were obtained, but when the Cu:substrate ratio increases, a sharp decrease in conversions takes place. The highest TON values (*ca.* 320 mol of aldehyde per 1 mol of Cu) were obtained with the highest catalyst to alcohol ratios applied, 1000 and 500, giving 34% and 69% conversion, respectively.

Other Oxidants

Other typical oxidants were also applied under similar reaction conditions as described above, the most suitable ones being air and H_2O_2 (Table 2). However with air the reaction proceeds slower than with O_2, due to reduced oxygen concentration and requires a longer reaction time (18 h). Interestingly, H_2O_2 also turned out to be an efficient oxidant and quantitative conversions were obtained using a slight excess of H_2O_2. Or-

Table 2. The effect of other oxidants (air, H_2O_2, *t*-BuOOH, NaOCl) on the oxidation of benzyl alcohol with TEMPO (5 mol%), $CuSO_4$ (1 mol%) and **L4** (2 mol%) in 0.1 M K_2CO_3.

Run	Oxidant	Amount/ equiv.[d]	Conv. [%]	Selectivity [%]	Time [h]
1	O_2	1 atm	100	99	2
2	air	1 atm	17	99	2
3	air	1 atm	99	99	18
4[a]	H_2O_2	0.5 mL/1.9 equiv.	62	99	2
5	H_2O_2	1 mL/3.8 equiv.	100	99	2
6[a]	*t*-BuOOH	0.55 mL/2 equiv.	19	99	2
7[a]	CHP[b]	1 mL/1.8 equiv.	25	99	2
8[a]	Oxone®[c]	3.7 g/2 equiv.	28	99	2
9[a]	NaOCl	1 mL	14	99	2

[a] Reactions carried out under an argon atmosphere.
[b] CHP = cumyl hydroperoxide.
[c] The active oxidant of Oxone® is $KHSO_5$.
[d] Equivalent of oxidant vs. substrate.

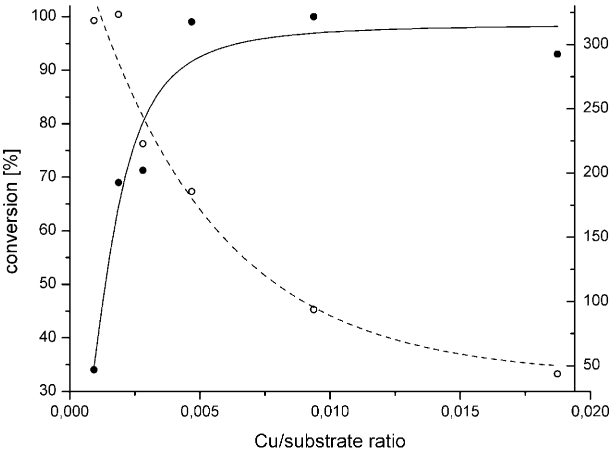


Figure 6. The effect of catalyst to substrate ratio on the TON (○, right axis) and conversion (●, left axis) in benzyl alcohol oxidation. *Conditions:* **L4**:$CuSO_4$ ratio = 2, otherwise same as in Figure 4.

ganic hydroperoxides like cumyl hydroperoxide or *tert*-butyl hydroperoxide proved to be poor sources of oxygen for the catalyst. Sodium hypochlorite and Oxone® gave similar results to the organic peroxides.

Oxidation of Other Substrates

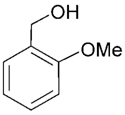
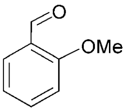
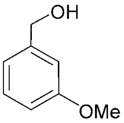
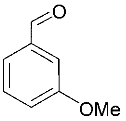
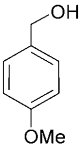
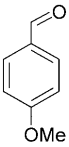
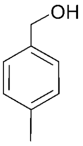
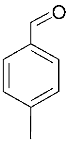
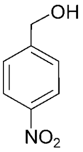
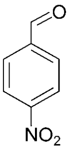
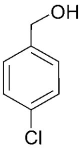
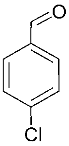
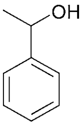
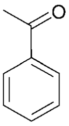
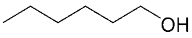
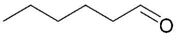
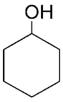
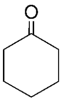
The aerobic oxidation of various alcohols in aqueous solution, catalyzed by the *in situ* made $CuSO_4$/**L4** (1:2) system afforded the corresponding carbonyl products as summarized in Table 3. Methoxy-substituted benzylic alcohols were oxidized to the corresponding aldehydes with good to excellent conversions (Table 3 runs 1–3) depending on the position of the MeO substituent – from the series the *para* MeO-substituted benzyl alcohol gave the lowest conversion (81%). Thus the influence of *para*-substitutents was further studied. Oxidation of benzyl alcohols having an electron-donating methyl group and electron-withdrawing NO_2 group gave similar conversions (88%), while the chlorine-substituted substrates gave slightly better yields (Table 3 runs 3–6). Interestingly, as the unsubstituted benzyl alcohol is oxidized with quantitative conversions, the influence of the remote *para*-substituent appears to be more related to steric effects than electronic ones. Secondary benzylic alcohols (here 1-phenylethanol) are also oxidized with good efficiency, while primary and secondary aliphatic alcohols were barely reactive.

Catalytic Active Species

Although the copper(II) 2-*N*-arylpyrrolecarbaldimino complexes can be synthesized in water and they are stable in various alcohol solutions, this seems not to be the case in alkaline aqueous solutions. For example, when pre-made **1** is immersed in a very dilute aqueous solution of K_2CO_3, the electrospray ionization-mass spectrometry (ESI-MS) measurements show, besides the dominating peak patterns of potassium carbonate clusters, moderate peaks at $m/z = 316$ and 332. According to the isotope distribution they can be assigned as $[C_{11}H_9N_2Cu + NaHCO_3 + H]^+$ and $[C_{11}H_9N_2Cu + KHCO_3 + H]^+$ cations, respectively (see Supporting Information). Simultaneously to them, peaks with high intensities corresponding to the copper complex with one ligand and increasing amounts of the carbonate adducts with potassium, sodium and hydrogen cations, were also observed. Such peak patterns are common during the electrospray ionization.[20] After addition of benzyl alcohol and TEMPO to the mixture of K_2CO_3 and **1** no peaks related to the substrate or TEMPO coordination could be identified. It is worthy of note that the identified complex cations in the MS appear formally as Cu(I) species and their formation is presumably related to the redox processes that can occur in the gas phase.[20] To summarize, in alkaline media one ligand from the initial complex has cleaved and this opens two new coordination sites at the Cu center.

To confirm the oxidation state of the complexes in alkaline solution and the redox behaviour of the catalytic systems during the oxidation, UV-vis studies were carried out. Accordingly, in alkaline solution and under atmospheric pressure of oxygen Cu(II) complexes are present. When benzyl alcohol is introduced under an argon atmosphere to the alkaline complex solutions, the Cu(II) complexes are reduced to Cu(I) species. In the presence of oxygen, these

Table 3. The oxidation of selected alcohols catalyzed by $CuSO_4$/**L4** 1:2 *in situ* system.[a]

Run	Substrate	Product	Time [h]	Conv. [%]	Selectivity [%]
1			2	94	>99
2			2	99	>99
3			2	81	>99
4			2	88	>99
5			2	89	>99
6			2	92	>99
7			20	68	100
8			20	6	100
9			20	3	100

[a] *Conditions:* 3 mmol of substrate, 5 mol% of TEMPO, 1 mol% of $CuSO_4$ and 2 mol% of **L4**, 1 atm of O_2.

Cu(I) species are oxidized back to Cu(II). This is an identical with the redox behaviour of previously reported Cu(II) diimine catalysts.[13c]

We have shown previously that in alkaline media the Cu(II) diimine catalysts are in dynamic equilibrium and various structures can be present at the same time depending on the ligand to metal ratio and pH.[13c,19d] The oxidation activity of these complexes was connected to the presence of (diimine)-Cu(II)$(OH)_2$ species. A similar equilibrium is to be expected also with **1**–**4** and a relatively high $[K_2CO_3]$ is needed for sufficient ligand dissociation which generates two coordination sites. After that the catalytic oxidation can proceed with a similar mechanism as previously proposed for other TEMPO/copper catalysts,[11,13] which might include simultaneous coordination of ligands, OH^-, TEMPO or benzyl alkoxide to Cu(II).[13]

The oxidation results above show higher activity for the *p*-Cl (**3**) and the *p*-F (**4**) substituted complexes compared to those bearing phenyl (**1**) and *p*-Me (**2**) substituents. Considering the ligand dissociation in alkaline solutions as a key transformation to generate the catalytic active species, the differences in catalytic activity can be rationalized. The electron-withdrawing substituents in **3** and **4** weaken the coordination of the imine moiety and thus promote the ligand dissociation. A marked difference between **3** and **4** in the solid state structures is the presence of an intermolecular H-bonding network of the *p*-Cl-substituents (see Supporting Information). The necessity to break down the hydrogen bonding network during the ligand dissociation could also explain the slow activation of pre-made **3**. In general, as the pre-made complexes has reduced solubility, the improved initial activity of the *in situ* made systems is most probably related to the instant formation of catalytic active species.

Conclusions

Although Cu(II) 2-pyrrolecarbaldimino complexes have been known for 80 years, this is the first example of their use as oxidation catalysts. It can be concluded that these unsymmetrical Cu(II) complexes introduce a new and highly efficient platform for the catalytic oxidation of benzylic alcohols in aqueous solutions. With these catalysts quantitative yields of benzaldehydes can be obtained using dioxygen, air or hydrogen peroxide as the end oxidants. This makes the system relatively cheap, flexible and environmentally benign. When compared to our previously reported Cu diimine catalysts, the catalysts described herein are more efficient and work under milder reaction conditions (low catalyst loadings, atmospheric pressure of O_2 or air and relatively low pH <11.5).

Experimental Section

General Remarks

All chemicals were purchased from commercial sources, and used without purification. IR analyses were performed on a Perkin–Elmer Spectrum One spectrometer. An EA 1110 CHNS-O CE instrument was used for elemental analysis. ^{1}H NMR spectra of synthesized ligands were collected using a Varian Gemini 200 spectrometer. A JEOL JMS-SX102 mass spectrometer was used for MS measurements. AAS measurements were performed using a Perkin–Elmer 3030 AA spectrophotometer.

Ligand and Complex Synthesis

The syntheses of 2-*N*-arylpyrrolecarbaldimine ligands and Cu(II) complexes **1–4** have been previously published.[21]

The new complex **5**, bis[2-*N*-(di-2,2-isopropylphenyl)-pyrrolylcarbaldimide]copper (II), was prepared with the same method. IR: $\nu = 1573$ cm-1 (C=N); elemental analysis calcd. (%) for $C_{34}H_{42}CuN_4$: C 71.61, H 7.42, N 9.82, found: C 71.52, H 7.73, N 9.43; MS (EI$^+$): *m*/*z* (%) = 569 (20, M^+-1), 316 (50, $M^+-C_{17}H_{21}N_2$), 253 (100 ,$C_{17}H_{21}N_2$).

Oxidation Experiments

Oxidation reactions were carried out in 25-mL, two-necked, round-bottom flasks equipped with condenser and connected to the balloon filled with O_2. The apparatus was evacuated and filled with O_2 (three times) before the experiment. For the *in situ* oxidation K_2CO_3 and $CuSO_4$ were added followed by the addition of TEMPO and the appropriate ligand. For the oxidation with bis-(2-*N*-phenyl)-pyrrolylcarbaldimide copper(II) complexes, an adequate amount of complex was used. Reagents were stirred for *ca.* 30 min prior to the addition of substrate for complex formation and pressure stabilization.

The desired reaction temperature was achieved using an oil bath. Dioxygen uptake was measured by the gas volumetric apparatus using a gas burette with levelling bulb filled with water.[22] The mole of gas reacted was calculated from the ideal gas equation using actual temperature and pressure values. Reaction mixtures after the oxidation reaction were neutralized by 1 M HCl, and then 10 mL of EtOAc were added for the extraction. The organic phase was used for chromatographic analyses.

Chromatographic Analyses

Reaction products were isolated and analyzed quantitatively by GC (Agilent 6890 chromatograph, Agilent 19091 J-413 capillary column 0.32 mm × 30 m × 0.25 μm, FID detector) using internal standards. Products were identified by GC-MS analyses (Agilent 6890N equipped with Agilent 5973 mass selective detector, HP 19091 L-102 capillary columns, 200 mm × 24 m × 0.31 μm).

Acknowledgements

The financial support of this work by the Magnus Ehrnhrooth Foundation (P.F.), the Fortum Foundation (A.S.) and the Academy of Finland (M.R. and M.L.) is gratefully acknowledged.

References

[1] a) G. Gillies, D. Donnecke, W. Imhof, *Monatsh. Chem.* **2007**, *138*, 683–686; b) D. Dallinger, C. O. Kappe, *Chem. Rev.* **2007**, *107*, 2563–2591; c) B. Cornils, W. A. Herrmann, (Eds.), *Aqueous-Phase Organometalic Catalysis*, Wiley, Weinheim, **1998**.

[2] a) R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley, Weinheim, **2007**; b) R. A. Sheldon, *Green Chem.* **2005**, *7*, 267–278; c) J. H. Clark, S. J. Tavener, *Org. Process Res. Dev.* **2007**, *11*, 149–155.

[3] a) R. Liu, Ch. Dong, X. Liang, X. Wang, X. Hu, *J. Org. Chem.* **2005**, *70*, 729–731; b) S. Kobayashi, *Adv. Synth. Catal.* **2002**, *344*, 219; c) R. A. Sheldon, *Chem. Commun.* **2008**, 3352–3365; d) K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry, M. Stefaniak, *Green Chem.* **2008**, *10*, 31.

[4] a) I. W. C. E Arends, R. A. Sheldon, *Modern Oxidation Methods*, (Ed.: J.-E. Bäckvall), Wiley, Weinheim, **2004**, p 83; b) S. Stahl, *Angew. Chem.* **2004**, *116*, 3480–3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420, and refer-

ences citied therein; c) *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, (Eds.: D. H. R. Barton et al.), Plenum Press, New York, **1993**; d) M. J. Schultza, M. S. Sigman, *Tetrahedron*, **2006**, *62*, 8227–8241; e) N. Jiang, A. J. Ragauskas, *Tetrahedron Lett.* **2007**, *48*, 273–276; f) S. S. Kim, H. C. Jung, *Synthesis* **2003**, 2135–2137; g) G-J. T. Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.

[5] a) W. Partenheimer, *Adv. Synth. Catal.* **2006**, *348*, 559–568; b) S. Stahl, *Angew. Chem.* **2004**, *116*, 3480–3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420; c) V. R. Choudhary, P. A. Chaudhari, V. S. Narkhede, *Catal. Commun.* **2003**, *4*, 171.

[6] a) R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977; b) A. Sheldon, I. W. C. E. Arends, G.-J. T. Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781; c) J.-M. Brégeault, *Dalton Trans.* **2003**, 3289; d) N. Jiang, D. Vinci, Ch. L. Liotta, Ch. A. Eckert, A. J. Ragauskas, *Ind. Eng. Chem. Res.* **2008**, *47*, 627–631; e) Ed. L. I. Simándi, *Advances in Catalytic Activation of Dioxygen by Metal Complexes*, Kluwer, Dordrecht, **2003**; f) I. P. Skibida, A. M. Sakharov, *Catal. Today* **1996**, *27*, 187–193; g) C. L. Hill, *Nature* **1999**, *401*, 436–437.

[7] *March's Advanced Organic Chemistry*, 5th edn., (Eds.: M. B. Smith, J. March), Wiley, New York, **2001**.

[8] a) B. P. Buffin, J. P. Clarkson, N. J. Belitz, A. Kundu, *J. Mol. Catal. A: Chem.* **2005**, *225*, 111–116; b) I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2002**, *344*, 355.

[9] a) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504–7507; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363; b) Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2007**, *9*, 3813.

[10] a) R. A. Sheldon, I. W. C. E. Arends, *J. Mol. Cat. A: Chem.* **2006**, *251*, 200–214; b) D. Geißlmeir, W. G. Jary, H. Falk, *Monatsh. Chem.* **2005**, *136*, 1591–1599; c) S. Striegler, *Tetrahedron* **2006**, *62*, 9109–9114; d) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071; e) L. Lin, J. Liuyan, W. Yunyang, *Catal. Commun.* **2008**, *9*, 1379–1382.

[11] a) P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, *Chem. Commun.* **2003**, 2414–2415; b) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2004**, *346*, 805–811.

[12] J. S. Uber, Y. Vogels, D. van den Helder, I. Mutikainen, U. Turpeinen, W. T. Fu, O. Roubeau, P. Gamez, J. Reedijk, *Eur. J. Inorg. Chem.* **2007**, *26*, 4197–4206.

[13] a) P. J. Figiel, M. Leskelä, T. Repo , *Adv. Synth. Catal.* **2007**, *349*, 1173–1179; b) P. J. Figiel, P. Lahtinen, M. Leskela, T. Repo, *Abstracts of Papers*, *233rd ACS National Meeting*, Chicago, IL, United States, March 25–29, **2007**, INOR-047; c) H. Korpi, P. J. Figiel, K. Kervinen, E. Lankinen, M. Leskelä , T. Repo, *Eur. J. Inorg. Chem.* **2007**, *26*, 2465–2471.

[14] B. Emmert, K. Diehl, F. Gollwitzer, *Ber. Dtsch. Chem. Ges.* **1929**, *62B*, 1733.

[15] a) C. N. Iverson, C. A. G. Carter, R. T. Baker, J. D. Scollard, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2003**, *125*, 12674–12675; b) R. Tewari, R. C. Srivastava, *Acta Crystallogr.* **1971**, *B27*, 1644–1649; c) A. Chakravorty, T. S. Kannan, *J. Inorg. Nucl. Chem.* **1967**, *29*, 1691–1699; d) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *Organometallics* **2001**, *20*, 4793–4799.

[16] V. V. Grushin, W. J. Marshall, *Adv. Synth. Catal.* **2004**, *346*, 1457–1460.

[17] K. N. Yeh, R. H. Barke, *Inorg. Chem.* **1967**, *6*, 830–833.

[18] C. M. Wansapura, C. Juyoung, J. L. Simpson, D. Szymansi, G. R. Eaton, S. S. Eaton, S. Fox, *J. Coord. Chem.* **2003**, *56*, 975–993.

[19] a) H. Korpi, P. Lahtinen, V. Sippola, O. Krause, M. Leskelä, T. Repo, *Appl. Catal. A: General* **2004**, *268*, 199–206; b) P. Lahtinen, H. Korpi, E. Haavisto, M. Leskelä, T. Repo, *J. Comb. Chem.* **2004**, *6*, 967–973; c) P. Lahtinen, E. Lankinen, M. Leskelä, T. Repo, *Appl. Catal. A: General* **2005**, *295*, 177–184; d) H. Korpi, V. Sippola, I. Filpponen, J. Sipilä, O. Krause, M. Leskelä, T. Repo, *Appl. Catal. A: General* **2006**, *302*, 250–256.

[20] a) R. Franski, *J. Mass Spectrom.* **2004**, *39*, 272–276; b) G. J. V. Berkel, *J. Mass Spectrom.* **2000**, *35*, 773–783.

[21] a) W. Addison, J. H. Stenhouse, *Inorg. Chem.* **1978**, *17*, 2161–2165; see also: b) A. Mohamadou, J-P. Barbier, M. Aplincourt, *J. Chem. Res.* **1998**, 140–141.

[22] a) B. Sun , J. Chen, J. Hu, X. Li, *J. Inorg. Biochem.* **2006**, *100*, 1308–1313; b) D. Chen, A. E. Martell, *Inorg. Chem.* **1987**, *26*, 1026–1030.