

Palladium-neocuproine catalyzed aerobic oxidation of alcohols in aqueous solvents

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Abstract

An overview is presented on the performance of Pd-complexes with phenanthroline-type ligands that are highly active catalysts for alcohol oxidation in water as well as in water/polar co-solvent mixtures. The mechanistic details of this intriguingly active and stable Pd-species are summarized. The (neocuproine)Pd(OAc)₂ catalyst is unique in that it tolerates water, polar co-solvents and a wide variety of functional groups in the alcohol. Turnover frequencies of >1500 h⁻¹ were achieved in the latter case and a series of alcohols was oxidized with 0.1–0.5 mol% of catalyst. © 2006 Elsevier B.V. All rights reserved.

Keywords: Palladium; Phenanthroline; Alcohol oxidation; Dioxygen; Water

1. Introduction

The oxidation of alcohols to carbonyl compounds is a pivotal reaction in the fine chemical industry. The classical methodology is based on the stoichiometric use of heavy metals, notably Cr and Mn [1,2]. Alternatively metal-free oxidation, such as the Swern and Pfitzner-Moffat protocols, is based on, e.g. dimethylsulfoxide as oxidant in the presence of an activating reagent such as *N,N*-dicyclohexylcarbodiimide, an acid anhydride or acid halide [3]. Although the latter methods avoid the use of heavy metals, they usually involve moisture-sensitive oxidants and environmentally undesirable reaction media, such as chlorinated solvents. The desired oxidation of alcohols only requires the formal transfer of two hydrogen atoms, and therefore the atom economy of these methods is extremely disadvantageous. Alternatively hypochlorite has proven to be a very useful oxidant in combination with 2,2,6,6-tetramethylpiperidiny (TEMPO) as a catalyst [4]. Also high valent ruthenium oxidants can be generated in situ using NaOCl [5]. However, in view of atom efficiency the use of oxygen or hydrogen peroxide as the final oxidant deserves preference. In this way water is the only by-product formed. In the last decade numerous articles have appeared, notably describing cobalt [6], copper [7], ruthenium [8], palladium [9,10] and platinum [11] catalyzed reactions with dioxygen as the terminal oxidant. When using

hydrogen peroxide as the oxidant, tungsten-based catalysts can be used [12]. In addition biocatalytic methods can be used to oxidize alcohols [13–15]. However, many of the catalytic systems mentioned above have a few drawbacks: (1) a low tolerance towards water, while by definition water is formed in the reaction; (2) a low tolerance towards functionalized alcohols [16]; (3) an (often) tedious work-up procedure with accompanying catalyst decomposition and (4) water-compatible systems, including biocatalytic systems, are usually slow. In this review we present an overview of the outstanding performance of water-stable palladium catalysts in the aerobic oxidation of alcohols.

2. Palladium-bathophenanthroline as a catalyst for alcohol oxidation

We wanted to design a catalyst that could reach high turnover frequencies for the aerobic alcohol oxidation when using water as a reaction solvent. When reviewing the literature, Pd demonstrates the highest stability in combination with an excellent activity. Following our achievements in the field of Pd-catalyzed hydroxycarboxylations, where sulfonated tris(triphenylphosphine)-palladium (TPPTS) was used as a recyclable highly active palladium catalyst in water [17], we started to explore analogous nitrogen ligated palladium complexes. These complexes were first used for the Wacker-type oxidation of alkenes [18]. Afterwards it was found that these catalysts were especially active in alcohol oxidation. The bathophenanthro-

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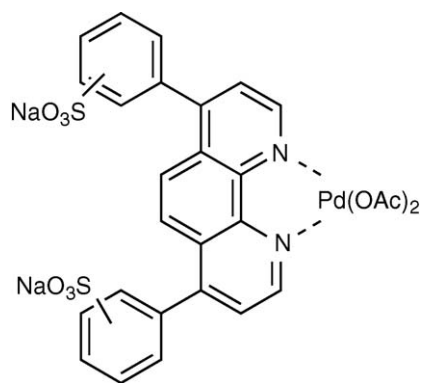


Fig. 1. Structure of the bathophenanthroline ligand.

Table 1
Oxidation of primary alcohols using a Pd(II)-bathophenanthroline catalyst in water

Substrate	Product	TOF _i (h ⁻¹)	Sel. (%)
		20	95
		21	97 ^a
		35	99
		20	89

0.25 mol% bathophen*Pd(OAc)₂, 0.5 eq. NaOAc, H₂O pH 11.5, T = 100 °C, p = 30 bar, t = 5 h.

^a TEMPO(4 eq) added.

line ligand (see Fig. 1) is commercially available and was tested on a range of alcohols. In Tables 1 and 2 the results are shown for the oxidation of primary alcohols and secondary alcohols, respectively. These results were obtained under the

optimized conditions as described in previous publications [19]. In general the system is highly active for both primary and secondary alcohols. The turnover frequencies (TOF) reached equal around 20 h⁻¹ for primary and 50 h⁻¹ for secondary alcohols. Aliphatic as well as benzylic and allylic alcohols demonstrate activities in the same range. Especially aliphatic aldehydes are not stable under these conditions and are further oxidized to the acids. The presence of small amounts of TEMPO (see entry 3 Table 1) prevents this, and aldehyde was formed selectively. What makes this system special is that the catalyst solution can be recovered after the reaction by simple phase separation and reused multiple times. The activity obtained for 2-hexanol oxidation was 49 h⁻¹ even after five times. The presence of two phases causes the reactivity to go down for heavier aliphatic alcohols which exhibit lower solubility in water: as can be seen in the range of cycloalcohols in Table 2, the reactivity goes down with an increase in carbon content.

The mechanism that was postulated based on our initial studies is shown in Fig. 2 [19b]. The reaction is half-order in palladium and first order in the alcohol substrate. The resting catalyst is a dimeric complex containing bridging hydroxyl groups. Reaction with the alcohol in the presence of a base, added as a cocatalyst (NaOAc) or free ligand, affords a monomeric alkoxy palladium(II) intermediate which undergoes β-hydride elimination to give the carbonyl compound, water and a palladium(0) complex. Oxidative addition of dioxygen to the latter affords a palladium(II) η-peroxy complex which can react with the alcohol substrate to regenerate the catalytic intermediate, presumably with concomitant formation of hydrogen peroxide as was observed in analogous systems. Recently, Stahl et al. conducted mechanistic studies on the Pd/DMSO and Pd/pyridine systems and found that both pyridine and DMSO had a positive influence on the reoxidation of palladium(0) [20].

The results of mechanistic studies which underline this mechanism are listed below.

Table 2
Oxidation of secondary alcohols using a Pd(II)-bathophenanthroline catalyst in water

	TOF _i (h ⁻¹)		TOF _i (h ⁻¹)		TOF _i (h ⁻¹)
	100		96		112
	49		99		52
	30		40		20
	20				67
	13				

0.25 mol% bathophen*Pd(OAc)₂, 0.5 eq. NaOAc, H₂O pH 11.5, T = 100 °C, p = 30 bar, t = 5 h.

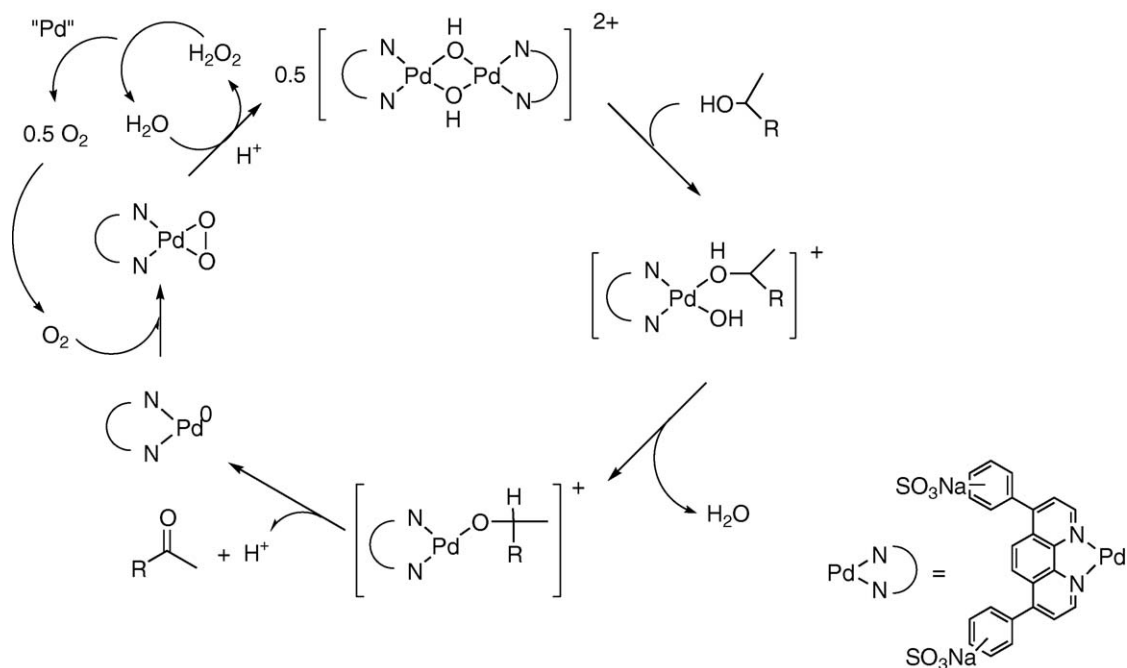


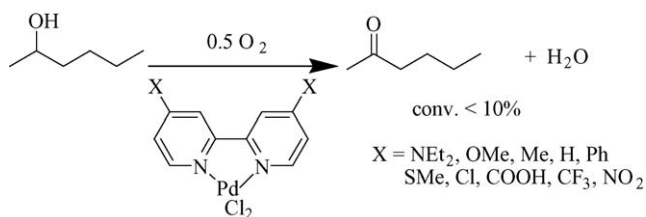
Fig. 2. Postulated mechanism for the Pd-phenanthroline catalyzed oxidation of alcohols.

- Kinetic studies reveal that the reaction is half-order in palladium. This would be consistent with the existence of palladium dimers in solution, which has been observed for a large number of palladium(II) diamine [21] or diimine [22] complexes. The precursor is a dihydroxy-bridged palladium dimer which is in equilibrium with its monomer.
- No base effect was present: Many alcohol oxidations are carried out in the presence of a substantial amount of base, because the reaction often involves abstraction of a proton from an alcohol coordinated to the metal centre. Although in initial experiments we carried out the palladium-catalyzed alcohol oxidation at pH around 11, later experiments showed that a high pH was not necessary for a smooth reaction. Addition of some sodium acetate was beneficial to the reaction by preventing palladium black formation. The lack of base effect was rather surprising. This led us to propose that coordinated hydroxide may abstract the proton from the alcohol, resulting in the palladium alkoxide species and water as the leaving group. This mechanism would not be acid/base dependent and would create a vacant site at palladium for β -hydride elimination [23].
- Coordinating anions were found to be necessary for stabilising palladium catalyst. Acetate and trifluoroacetate were beneficial to the reaction, giving the highest rates without palladium black formation. More tightly coordinating anions such as chloride and acetylacetonate retarded the reaction to a certain extent, while Pd(0) was still efficiently recycled to Pd(II). On the other hand, when non-coordinating anions such as perchlorate, tetrafluoroborate or triflate were used essentially all the palladium decomposed to palladium black and much less ketone was formed.
- Preference of primary alcohol over secondary alcohol was detected in competition experiments. This phenomenon hints at the presence of a metal-alkoxy species as an intermediate in the catalytic cycle. This preference is possibly due to a combination of decreased steric hindrance of the coordinated primary alkoxy group compared to the secondary alkoxy group and higher acidity of the primary alcohol. These experiments were performed using intramolecular competition in bifunctional (i.e. 5-hydroxy-hexanol) substrates as well as intermolecular competition using sulfonated alcohols.
- Kinetic isotope effects observed for benzylic and aliphatic alcohols range from 1.2 to 2.1. The fact that such a small KIE was observed indicates that β -hydride elimination could be rate-limiting.
- The oxygen pressure had little influence on the reaction under our conditions, which indicates that reoxidation during catalysis occurs after the rate-limiting step. However, it is necessary to apply oxygen pressure in the aqueous reaction system, because the solubility of dioxygen in water is about an order of magnitude lower than in organic solvents.

3. Electronic effects

To obtain more detailed information about the nature of the rate-limiting step and to discover more active catalysts a range of 4,4'-disubstituted-2,2'-bipyridines were investigated as ligands for the palladium-catalyzed aerobic oxidation of 2-hexanol

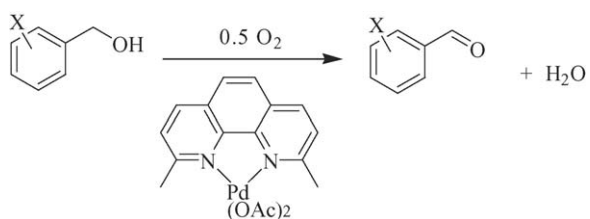
(Eq. (1)) [24].



(1)

Variation of the electron density on the diimine ligand changes the redox properties of the ligand. Therefore, this variation should provide evidence for whether an oxidation or a reduction step is rate-limiting. The reoxidation step of Pd(0) to Pd(II) should be facilitated by electron-donating substituents. On the other hand, if the reduction step is rate-limiting, then the reaction should be facilitated by electron-withdrawing substituents in the ligand. Because not all the catalysts were soluble in neat water, reactions were carried out in a DMSO/H₂O (1:1) mixture. It was observed that the reaction rate increases with electron-withdrawing substituents ($\rho = >0.18$) on the ligand [24]. This is consistent with the reduction of (bipy)Pd(II) to (bipy)Pd(0) or [(bipy)PdH]⁺ being rate-limiting (Fig. 3).

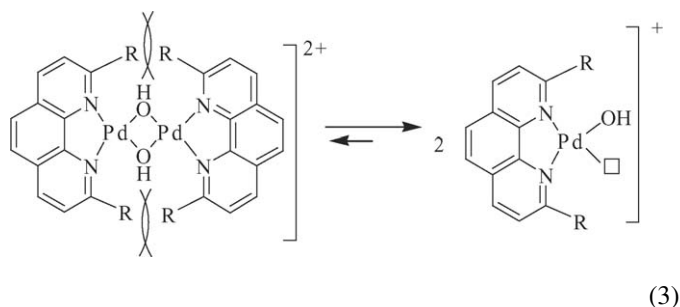
In a second approach to obtain electronic mechanistic information, a range of *meta*- and *para*-substituted benzylic alcohols was tested in the (neocuproine)Pd(OAc)₂ catalyzed oxidation (see Eq. (2)). In this case, the Hammett plot reveals a moderate ρ -value of -0.58 , which excludes benzyl cations as intermediate. Thus electron-donating substituents favour the reaction, which is in accordance with β -hydride being rate-limiting, as shown in Fig. 3.



(2)

We envisaged that we could obtain a more active catalyst and improve the substrate tolerance with the introduction of bulky groups on the 2- and 9-positions of the bathophenanthroline ligand. As already mentioned many diamine [21], diimine [22] but also diphosphine [25] complexes of palladium (and platinum) exist in solution as dimeric species. For instance, when dissolved in neutral aqueous solution, phenanthroline complexes of

palladium acetate form dihydroxo-bridged dimers [26]. Kinetic investigations of our aqueous biphasic catalytic system based on Pd/PhenS*, revealed that only a small fraction of the palladium dimers is dissociated during the reaction [19b]. Possibly, steric hindrance on the 2- and 9-positions of the bathophenanthroline ligand could enhance the reactivity of the catalyst, through facilitating the dissociation of the palladium dimer into the two (active) monomers (Eq. (3)).

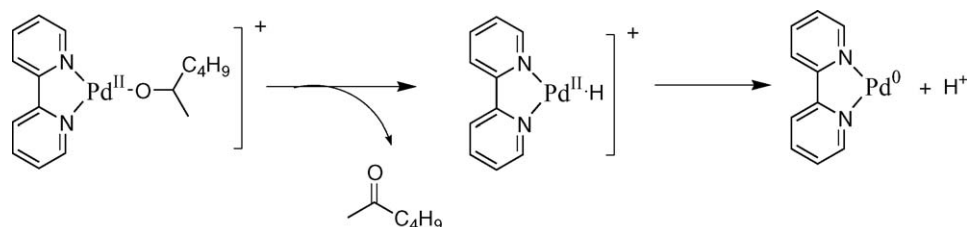


(3)

In an initial study a small selection of water-soluble phenanthroline derived ligands was investigated as ligands for the palladium catalyzed aerobic oxidation of 2-hexanol in an aqueous biphasic medium (see Fig. 4) [27].

When the commercially available water-soluble bathocuproine ligand was used in combination with Pd(OAc)₂, the activity was tripled to TOF = 150 h⁻¹. This result is in agreement with our working-hypothesis that dissociation of the palladium dimer is facilitated as a result of which activity increases. In the analogous (2,9-dimethylphenanthroline)platinum dimer, the methyl groups induce a significant repulsive interaction with the hydroxo-bridges and a small repulsive interaction with the opposite methyl groups [28]. The consequence of these steric effects is that the dimeric complexes bend from planarity and form a bowl-shaped dimer. In the oxidative carbonylation of phenol [29] and in CO [30] and alcohol [31] oxidations catalyzed by palladium-phenanthroline complexes in water an increased reaction rate with increasing steric bulk of the 2,9-disubstituted phenanthroline ligand has been observed. This might at least in part be ascribed to facilitated dissociation of the palladium dimer.

However, with the two sulfonated phenyl rings placed at the 2- and 9-positions instead of the 4- and 7-positions of phenanthroline, the palladium complex was completely inactive. This is possibly due to coordination of the sulfonate groups to the metal or due to metallation of a phenyl ring by the palladium. But, as no apparent changes of the catalyst solution were observed by UV-vis, we propose that an effective

Fig. 3. Rate-limiting β -hydride elimination step.

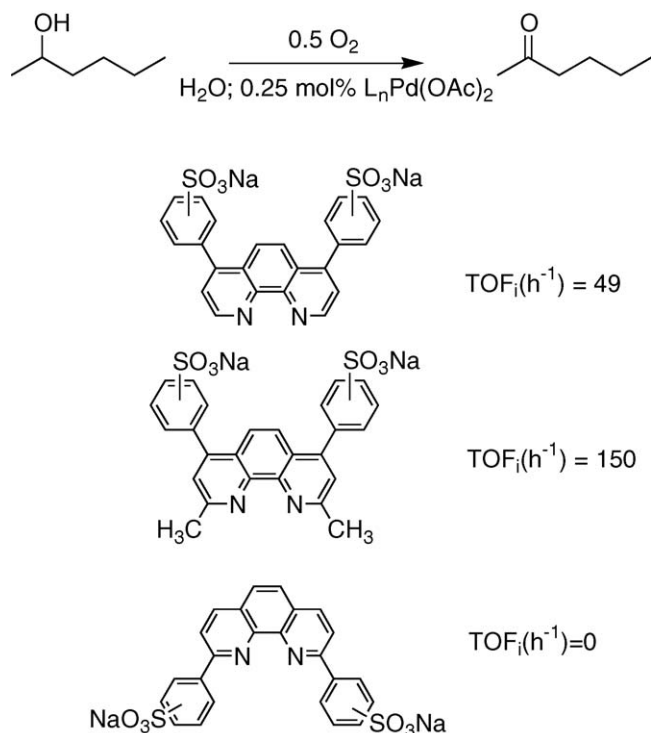


Fig. 4. Screening of water-soluble phenanthroline ligands used for initial studies.

shielding of the catalyst by the large phenyl rings takes place [32].

An extensive library of 2-substituted and 2,9-disubstituted phenanthroline ligands was synthesized, to identify a potential optimum in steric hindrance of ligands that, on the one hand, facilitate dissociation of the palladium dimer, but on the other hand do not hinder approach of the substrate alcohol too severely. Furthermore, the use of electron-withdrawing substituents on

the ligand (see above) could increase the activity of the catalyst even further. For synthetic considerations we chose to prepare non-sulfonated phenanthroline derivatives. At this stage we introduced a water/DMSO mixture (e.g. 1:1, v/v) as the reaction medium that conveniently dissolved all of these palladium complexes. The catalysts were thus tested in the aerobic oxidation of 2-hexanol in a parallel fashion and in a single liquid phase reaction (Fig. 5) [27].

Fig. 5 shows that in this series, by far, neocuproine is the best ligand for alcohol oxidation with palladium. With longer *n*-alkyl substituents on the ligand the reaction rates decreased considerably to circa 110 h^{-1} . When phenyl rings were placed at the 2-positions of phenanthroline, a similar (low) reactivity was observed compared to unsubstituted (phen) $\text{Pd}(\text{OAc})_2$ catalyst, which is remarkable. Contrary to our expectations, the ligands with electron-withdrawing substituents performed poorly. The 2,9-dichlorophenanthroline – although approximately similar in steric size as neocuproine – gave a poorly reactive complex, which might be attributed to the relatively reactive chloro substituents being replaced by other groups [33]. The trichloromethyl and trifluoromethyl groups are more stable electron-withdrawing substituents, and indeed with 2,9-bis(trifluoromethyl)phenanthroline and monosubstituted 2-(trichloromethyl)phenanthroline better results were obtained. With the bulkier 2,9-bis(trichloromethyl)phenanthroline, the complex was inactive. Lastly, the ligand with the electron-withdrawing carboxylate substituents formed moderately active complexes with $\text{Pd}(\text{OAc})_2$. Although these substituents might assist somehow in deprotonation of the alcohol, a clear beneficial effect was not observed. A striking result shown in Fig. 5 is that the reaction proceeds very well without any ligand present. Normally, such a reaction does not proceed in neat water because unreactive palladium black is formed after one cycle. However, in water/DMSO (1:1) the reaction is catalytic in simple $\text{Pd}(\text{OAc})_2$. This is in accordance with previous studies where

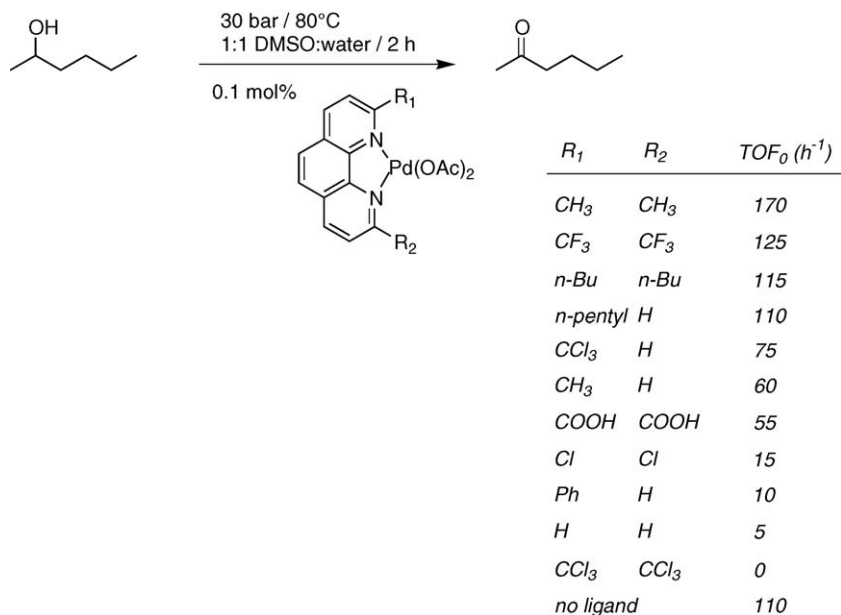


Fig. 5. Screening of substituted phenanthrolines in the Pd-catalyzed oxidation of alcohols in water/DMSO mixtures.

the salt has already been shown to be active in the oxidation of alcohols when neat DMSO was used as solvent [9]. Stahl et al. observed some deactivation of the catalyst in neat DMSO when 1 bar of dioxygen was used as the terminal oxidant [20a]. Under the high oxygen pressures (30 bar air) that we used the water/DMSO solution remained bright yellow and no Pd(0) was formed.

4. Solvent effect

It has to be emphasized that DMSO is not unique in its properties as the solvent. Initially the choice to use DMSO as a co-solvent was rather arbitrary. A range of other water-miscible co-solvents in a 1:1 (v/v) ratio with water was tested in the oxidation of 2-hexanol [27]. Fig. 6 shows that not only water/DMSO mixtures lead to high catalyst activity (TOF = 170 h⁻¹). Comparable reaction rates of TOF = 170 h⁻¹ were obtained when NMP was used as co-solvent. Also in the other co-solvents containing an amide functionality good reactivity (TOF ~120 for DMAC and ~85 h⁻¹ for DMF) was found. However, when the reaction was carried out in DMF the reaction rate was nearly zero on a few occasions, possibly due to well-known decomposition of this solvent in CO and HNMe₂. In all these cases a bright yellow solution was obtained after reaction. In ethylene carbonate, on the other hand, the initially bright yellow solution turned brown-black. Still, the catalyst maintained good activity (TOF ~140 h⁻¹). When sulfolane was used as a (1:1) co-solvent with water the reaction rate was very low and in some reactions an orange precipitate was formed. The main benefit of these co-solvents seems to come from an increased solubility of the substrate. This was substantiated by studies in which the water/DMSO fraction was varied.

Using the (neocuproine)Pd(OAc)₂ catalyst in neat water a TOF of 50 h⁻¹ was reached at 80 °C. Addition of small amounts (5–10 vol%) of DMSO had little effect [27]. Combined with the results from Fig. 6 this indicates that DMSO does not necessarily play a special role in (neocuproine)Pd(OAc)₂ catalyzed alcohol oxidations, as DMSO is believed to do in Pd(OAc)₂ catalyzed reactions [20a]. An increase in the DMSO fraction also leads to increased solubility of 2-hexanol in the ‘aqueous’ phase where the catalyst resides. In this way the reaction rate increased to an optimum rate of circa 170 h⁻¹ at 50–60% DMSO. At higher DMSO fractions the reaction rate decreased

significantly to a (relatively) low 70 h⁻¹ in neat DMSO. Several explanations can be envisaged for this decrease. First, the polarity of water ($\epsilon \sim 78$) is considerably higher than that of DMSO ($\epsilon \sim 48$). High polarity of the solvent is usually beneficial to oxidation reactions. Second, it is likely that DMSO is able to compete with the alcohol or hydroxide for coordination to the (neocuproine)Pd²⁺ center at high DMSO concentrations. When only 0.05 mol% catalyst was used instead of 0.1 mol% catalyst, the turnover frequency increased by a factor of circa 1.5 for the reaction catalyzed by (neocuproine)Pd(OAc)₂ in DMSO. This reflects the order of 1/2 in catalyst concentration also found earlier for the (PhenS*)Pd(OAc)₂ catalyzed alcohol oxidation [19b]. This order of 1/2 is a consequence of the catalyst being a palladium dimer, which is in equilibrium with 2 equivalents of an active palladium monomer.

5. Substrate scope

To determine the substrate scope a series of alcohols (primary, secondary, aliphatic, cyclic, allylic and benzylic) was tested in a water/DMSO (40:60) mixture. Reactions were performed for 4 h. Table 3 shows a selection of functionalized alcohols that are selectively oxidized by (neocuproine)Pd(OAc)₂. Apolar substrates, such as cyclododecanol, diphenylmethanol, and menthol reacted quickly. The allylic alcohol 1-octen-3-ol was oxidized to the enone. The reaction rate decreased to a certain extent due to competing coordination of olefin and alcohol functionalities [34]. Strikingly, however, when the olefinic group was farther removed from the alcohol functionality as for 1-dodecen-11-ol, the catalyst selectively oxidized the alcohol functionality. This is somewhat surprising, because the (PhenS*)Pd(OAc)₂ catalyst in water selectively converted the olefinic group to form 11-hydroxy-2-dodecanone (Wacker-type reaction), and afterwards converted the ketoalcohol into 2,11-dodecanedione [19b]. Probably, the substrate selectively coordinated via the olefinic moiety, but the presence of the two methyl substituents on the ligand prevented the substrate from turning into the plane of the catalyst for *cis*-hydroxypalladation [35]. Alternatively, a completely different catalytic species than the mononuclear palladium–phenanthroline complex suggested above in completely aqueous systems could be present. The distinctive influence of coordinating solvents could point in the direction of palladium-nanoparticles [36]. Further studies are needed to investigate the identity of the active species under water/co-solvent conditions.

The propargylic alcohol behaved similarly to the allylic 1-octen-3-ol, but increased electronegativity and possibly stronger coordination of the C≡C bond to palladium caused a slow conversion to the corresponding ynone. For the reactivity of primary alcohols, allylic cinnamyl alcohol was oxidized to cinnamaldehyde, which was far less susceptible to autoxidation. Even under an oxygen atmosphere and without addition of TEMPO the product remained stable. The diol *cis*-1,2-bis(hydroxymethyl)cyclohexane was also oxidized to the (mono-)aldehyde, but formed a lactol after intramolecular ring closure. This lactol was partly further oxidized to the lactone. A

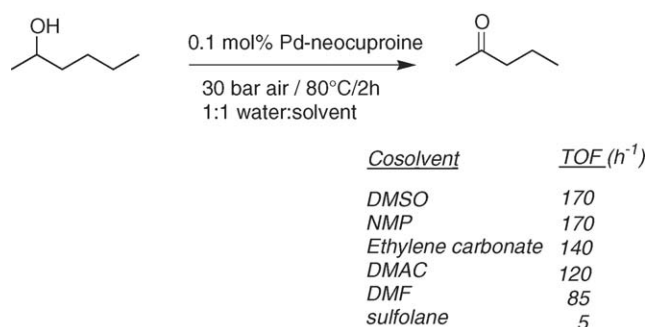
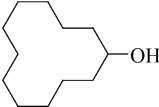
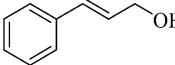
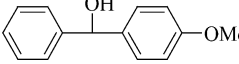
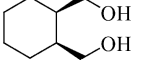
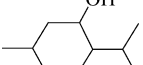
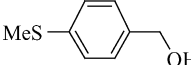
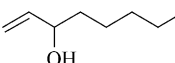
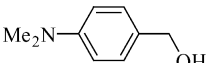
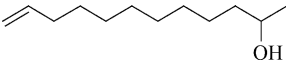
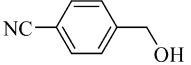
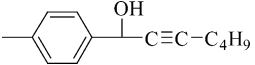
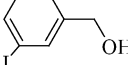
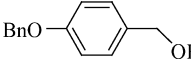


Fig. 6. Effect of solvent on the Pd(neocuproine)(OAc)₂ catalyzed oxidation of 2-hexanol in water/co-solvent mixtures.

Table 3
Substrate scope in the Pd(II)-neocuproine catalyzed oxidation of alcohols in water/DMSO

Substrate	Conv. (%)	Sel. (%)	Substrate	Conv. (%)	Sel. (%)
	58	100		28	100
	100	100		75	99
	71	100		86	100
	30	95+		60	99
	30	99+		37	100
	15	100		22	100
				90	99

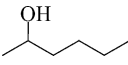
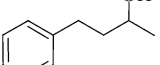
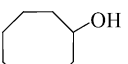
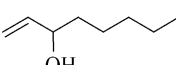
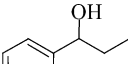
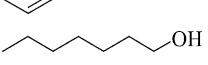
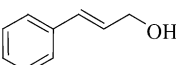
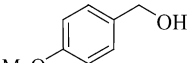
Typical conditions: 4 h; 0.5 mol% (neocuproine)*Pd(OAc)₂; 80 °C; 30 bar air; water/DMSO (40:60).

tolerance towards thioethers, tertiary amines and nitriles could be demonstrated: *p*-thiomethyl and *p*-dimethylaminobenzyl alcohol were quickly converted to the corresponding benzaldehydes. Benzyl alcohols with a *p*-cyano substituent could be oxidized as well, albeit slowly, due to the electron-withdrawing properties of the substituents. The catalyst also tolerated halides in the substrate, even the relatively sensitive iodide group in *m*-iodobenzyl alcohol was not attacked.

6. Optimized reactions

The previously reported system in water has the disadvantage of limited solubility of many substrates in neat water. A second and more general disadvantage from which nearly all catalyst systems seem to suffer, is the low tolerance for (coordinating) functional groups in the solvent or the substrate. The bathophenanthroline-Pd(OAc)₂ system, for example, could only tolerate a single ether functionality (in butyl proxitol), and all other functional groups proved insurmountable, as these coordinated more tightly to palladium [19b]. With an optimized system in hand, we are now capable of oxidizing a wide range of – also functionalized – alcohols. The large scale (20 mmol) reactions were carried out in a conventional autoclave at 100 °C and with 0.1 mol% (neocuproine)Pd(OAc)₂ (Table 4). Secondary aliphatic alcohols reacted very quickly to give the corresponding ketones, and occasionally some dehydrogenation of the ketones took place. It is noteworthy that under these conditions 2-hexanol is converted at rates *two orders of magnitude faster* than with existing catalytic methods [6–9]. With 0.005 mmol (0.025 m%) (neocuproine)Pd(OAc)₂ catalyst, the turnover frequency increased even further to ca. 1800 h⁻¹! Allylic primary

Table 4
Optimized conditions in the Pd(II)-neocuproine catalyzed oxidation in water/DMSO

Substrate	<i>t</i> (h)	TOF ₀ (h ⁻¹)	Conv. (%)	Sel. (%)
	2	≫500	100	100
	2	≫500	99	99
	3	400	93	99+
	3	400	95	96
	3	300	80	99+
	2.5	200	40	75 (heptanoic acid)/20 (heptanal)
	10	135	88	99+
	3	≫330	100	100

Conditions: 0.1 mol% (neocuproine)*Pd(OAc)₂; 100 °C; 50 bar 8% O₂; 1:1 water/DMSO.

alcohols can be oxidized smoothly, whereas primary aliphatic alcohols are oxidized to a mixture of aldehyde and acid. Notably, aldehydes can be produced selectively by adding TEMPO. In conclusion the use of a neocuproine ligand for the Pd-catalyzed oxidation of alcohols in water/co-solvent mixtures, in which the co-solvent can be DMSO, NMP, ethylene carbonate or DMAC, delivers a system that tolerates many sensitive or coordinating functional groups: C=C bonds, C≡C bonds, halides, α-carbonyls, ethers, thioethers, silyl ethers, sulfoxides, sulfones, sulfonates, amines, cyanides, amides, carbonates and esters. We expect that the catalyst system will have broad synthetic utility.

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