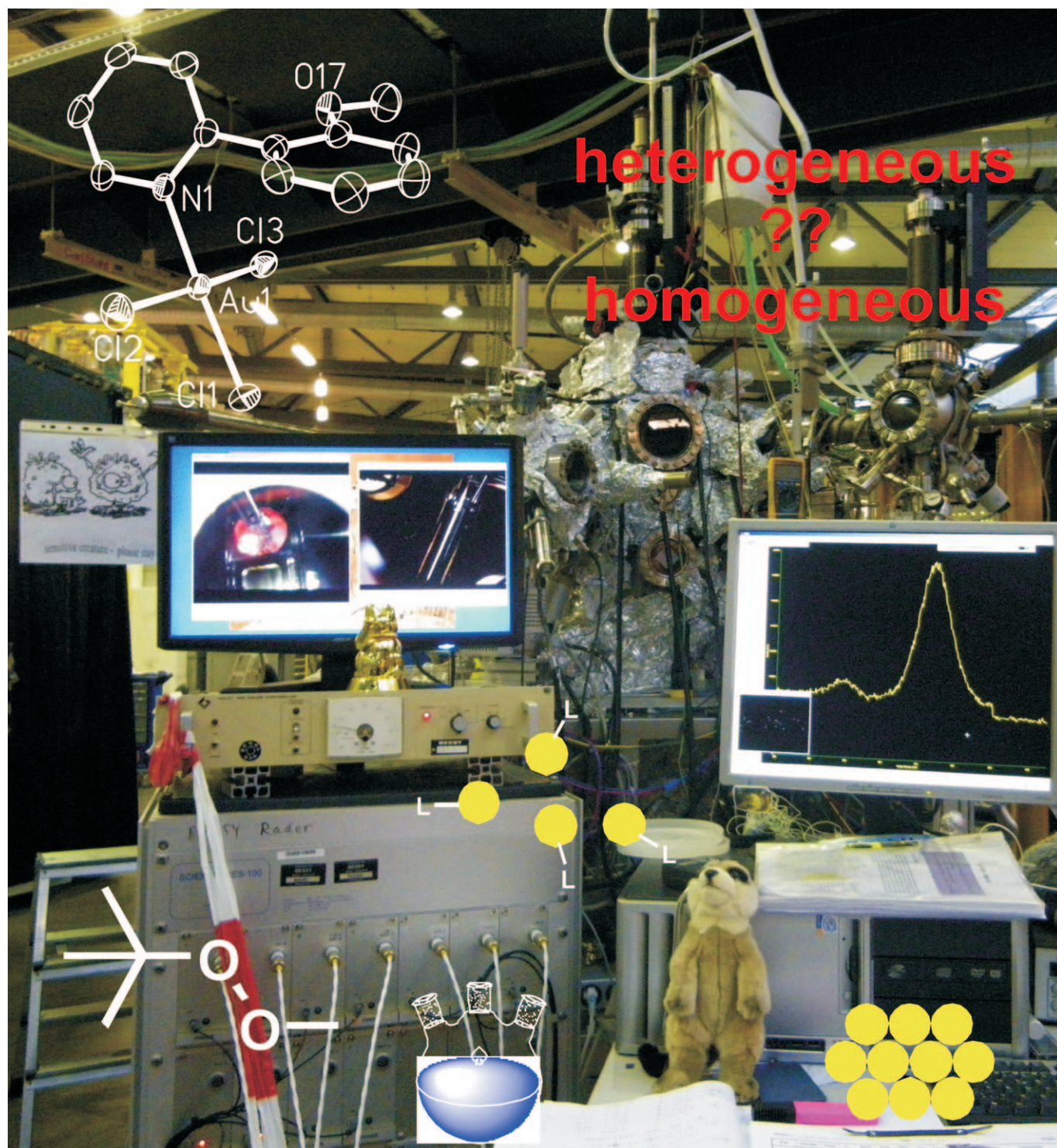


# Gold Catalysis: In Situ EXAFS Study of Homogeneous Oxidative Esterification\*\*

A. Stephen K. Hashmi,<sup>\*,[a]</sup> Christian Lothschütz,<sup>[a]</sup> Martin Ackermann,<sup>[a]</sup> René Doepp,<sup>[a]</sup>  
Sankaran Anantharaman,<sup>[b]</sup> Benjamin Marchetti,<sup>[b]</sup> Helmut Bertagnolli,<sup>\*,[b]</sup> and  
Frank Rominger<sup>[a]</sup>



**Abstract:** Gold complexes were prepared and investigated as catalysts for the oxidative esterification of aldehydes. Stabilisation by pyridine ligands gave good conversions and the in situ extended X-ray absorption fine structure (EXAFS) study of the reactions indicated that the reaction mixtures contained only mononuclear gold species. Thus, this is the first proof for a homogeneous gold-catalysed oxidation reaction; the presence of nanoparticles could be excluded experimentally.

**Keywords:** esters • EXAFS spectroscopy • gold • oxidation • pyridines

## Introduction

In the last few years, gold-catalysed organic transformations have become important tools to build up molecular diversity. Most of the reported reactions deal with cycloisomerisations or the activation of alkynes and allenes towards nucleophilic attack.<sup>[1]</sup> In contrast, there are only a few examples of gold-catalysed homogeneous oxidations. In 2005, Shi et al. reported the oxidation of alcohols to aldehydes and ketones with a homogeneous gold catalyst and oxygen as the oxidant.<sup>[2]</sup> In another publication they described the gold-catalysed oxidative cleavage of double bonds.<sup>[3]</sup> Additionally, Yuan and Bian published the oxidation of sulfides to sulfoxides by reductive hydrolysis of Au<sup>III</sup> sulfide complexes generated in situ.<sup>[4]</sup> They derived a mechanism based upon kinetic studies, as well as upon investigations from the Hill group.<sup>[5,6]</sup> Furthermore, there have been publications that dealt with oxidative-coupling reactions.<sup>[7]</sup> Inspired by a number of heterogeneous gold-catalysed oxidations, we began to investigate homogeneous oxidations catalysed by gold complexes.<sup>[8]</sup>

In our opinion, one of the most interesting reactions with regard to synthesis is the direct conversion of aldehydes and alcohols to the respective esters.<sup>[9]</sup> Hence, our aim was to establish a homogeneous gold-catalysed version of this reaction. A series of experiments with the “homogeneous” gold catalysts discussed above, in our hands, all showed a massive precipitation of elemental gold, even when conducted by several different co-workers. Thus, we were unconvinced as to whether these “homogeneous” oxidations are really catalysed by soluble mononuclear gold complexes. Many of the reactions may form gold nanoparticles in situ and then the

latter could be responsible for the detected oxidation activity, as known from heterogeneous gold catalysis. Thus, our work is aimed at the first proof of a truly homogeneous oxidation catalysed by mononuclear gold complexes.

## Results and Discussion

We selected to study a reaction of broad interest, namely oxidative esterification. In an initial screening, we used *p*-methoxybenzaldehyde, *n*-butanol and *tert*-butyl hydroperoxide (TBHP) as a test system with a series of different Au<sup>III</sup> salts (Figure 1). Of the catalyst systems tested, compounds

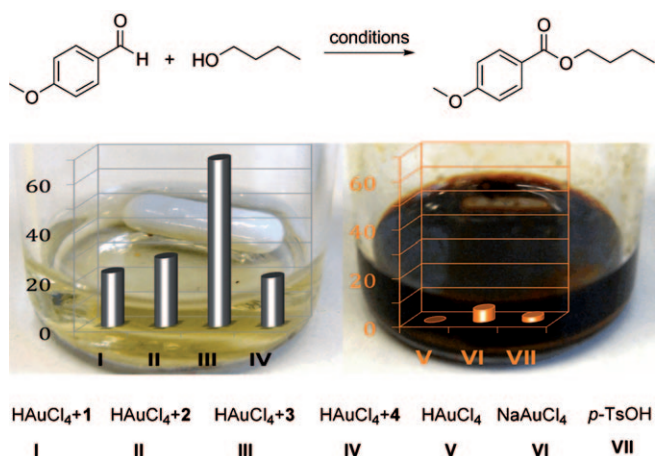


Figure 1. Picture of reaction flasks after the reaction has taken place with different catalyst systems (% yield). Left: stabilised conditions (pyridines **1–4**; **I–IV**). Right: non-stabilised conditions (**V–VII**). Reaction conditions: HAuCl<sub>4</sub> (4.50 mol %), pyridine compound (9 mol %), aldehyde (1.00 mmol), *n*-butanol (3.00 mmol), TBHP (1.50 mmol). For conditions **VII** 10 mol % of catalyst was used.

of Au<sup>I</sup> and Au<sup>III</sup> that contained ligands such as phosphines, phosphites and mono- and bidentate nitrogen-donor ligands delivered poor results and were accompanied by the formation of gold-black precipitate. The use of pyridine additives as stabilising agents led to a successful outcome and substitution at the 2-position turned out to be the most effective (Scheme 1).

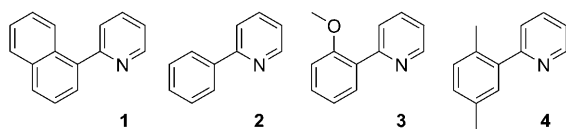
With the use of air or oxygen, auto-oxidation to the acid was observed. Other oxidants, such as hydrogen peroxide or cumene hydroperoxide, were inferior to TBHP. Following these findings, we extended the Au<sup>III</sup>-catalysed oxidative

[a] Prof. Dr. A. S. K. Hashmi, Dipl.-Chem. C. Lothschütz, Dipl.-Chem. M. Ackermann, Dipl.-Chem. R. Doepp, Dr. F. Rominger  
Institute of Organic Chemistry, University of Heidelberg  
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)  
Fax: (+49) 6221-544205  
E-mail: hashmi@hashmi.de

[b] S. Anantharaman, Dipl.-Chem. B. Marchetti, Prof. Dr. H. Bertagnolli  
Institut of Physical Chemistry, University of Stuttgart  
Pfaffenwaldring 55, 70569 Stuttgart (Germany)  
Fax: (+49) 711-6856-4443  
E-mail: h.bertagnolli@ipc.uni-stuttgart.de

[\*\*] EXAFS = extended X-ray absorption fine structure.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200903450>.



Scheme 1. Pyridines used as stabilising agents.

esterification to the conversion of either an aldehyde and an alcohol or two alcohols into the respective esters. Unfortunately, the use of two different alcohols led to inseparable mixtures of products, therefore, we decided to focus on the coupling of aldehydes and alcohols (Table 1). The reactions took place at relatively mild temperatures and could be run without solvent in most cases. Electron-rich and neutral aromatic aldehydes delivered good to excellent yields (Table 1, entries 1–6). A comparison of our synthesis of **5a** (Table 1, entry 1) with the literature<sup>[10–13]</sup> shows that, in one case,<sup>[10]</sup> a yield of 100% was reported for catalysis of the reaction with  $V_2O_5/H_2O_2$  (4 mol %). In a further case,<sup>[11]</sup> 91% yield of **5a** was obtained with 5 mol %  $[Cu(ClO_4)_2]/5$  mol %

Table 1. Formation of *n*-butyl esters **5** from various aldehydes.

| $R-\text{CHO} + \text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{conditions}} R-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ |   |           |                          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|-----------|--------------------------|
| Entry                                                                                                                                                                     | R | Product   | Yield [%] <sup>[a]</sup> |
| 1                                                                                                                                                                         |   | <b>5a</b> | 90                       |
| 2                                                                                                                                                                         |   | <b>5b</b> | 74                       |
| 3                                                                                                                                                                         |   | <b>5c</b> | 78                       |
| 4                                                                                                                                                                         |   | <b>5d</b> | 72                       |
| 5                                                                                                                                                                         |   | <b>5d</b> | 66 <sup>[b]</sup>        |
| 6                                                                                                                                                                         |   | <b>5e</b> | 68                       |
| 7                                                                                                                                                                         |   | <b>5f</b> | 32                       |
| 8                                                                                                                                                                         |   | <b>5g</b> | 48                       |
| 9                                                                                                                                                                         |   | <b>5h</b> | 60 <sup>[c]</sup>        |
| 10                                                                                                                                                                        |   | <b>5i</b> | 47 <sup>[d]</sup>        |

Typical conditions:  $HAuCl_4$  (4.50 mol %), **3** (9 mol %), aldehyde (1.00 mmol), alcohol (3.00 mmol), TBHP (1.50 mmol), 12 h, 55–75°C. [a] Isolated yield. [b] 1.00 mmol of TBHP was used. [c] Product could not be isolated in pure form. [d] Product is a 10:1 mixture of *trans* and *cis* isomers.

$InBr_3/TBHP$ . In both cases, the reaction conditions are harsh, either the reaction medium contains 70%  $HClO_4$ <sup>[10]</sup> or the reaction is conducted at 100°C.<sup>[11]</sup> Thus, our method delivers a similar yield of **5a** to the literature, but our reaction conditions are much milder, hence, a higher tolerance of functional groups is granted. Another comparison can be made for the synthesis of **5e** (Table 1, entry 6). Once again 100% yield has been reported after catalysis with  $V_2O_5/H_2O_2$  (4 mol %).<sup>[10]</sup> More representative are the values reported for reaction with Oxone in DMF at RT (19% yield),<sup>[12]</sup> with palladium/phosphinous acid/ $PhSi(OMe)_3$ /tetrabutylammonium fluoride (TBAF) (61% yield)<sup>[13]</sup> and with copper perchlorate/TBHP/ $InBr_3$  at 100°C (68% yield).<sup>[11]</sup> For this compound, our yield is the best reported so far and our reaction conditions are the mildest, which guarantees a high functional group tolerance and avoids exotic oxidants, such as  $PhSi(OMe)_3$ . The formation of **5a** by our method can be directly compared with heterogeneous catalysis by a  $TiO_2$ -supported gold catalyst<sup>[9a,14]</sup> (90 versus 79%). Other examples of gold-catalysed oxidation delivered aldehydes and only traces of esters,<sup>[9b]</sup> or carboxylic acids.<sup>[9c]</sup> In recent years, gold catalysts had proven to be superior to other metals in these heterogeneous oxidations.<sup>[1a,15]</sup>

The use of 1 equiv of TBHP delivered comparable results to the use of 1.5 equiv (Table 1, entry 4 versus 5), which indicated that oxidation of the alcohol is much slower than transformation of the hemiacetal formed in situ to the ester. The reaction of 2,4,6-trimethylbenzaldehyde (Table 1, entry 3) shows that even sterically hindered aldehydes can be transformed into the respective esters in good yield. For this transformation to **5c** we achieved a yield of 78%, one of the highest reported in literature.<sup>[16]</sup> When electron-deficient benzaldehydes were used (Table 1, entries 8 and 9), acetal formation caused a problem.

We also tested the variability of the alcohol component. Whereas primary alcohols furnished good results (Table 2, entries 1–3), the increased steric demand of secondary alcohols and the weaker nucleophilicity diminished the isolated

Table 2. Formation of esters **6** from 2-naphthaldehyde.

| $\text{2-naphthaldehyde} + \text{HO}-R \xrightarrow{\text{conditions}} \text{2-naphthaldehyde ester}$ |   |           |                          |
|-------------------------------------------------------------------------------------------------------|---|-----------|--------------------------|
| Entry                                                                                                 | R | Product   | Yield [%] <sup>[a]</sup> |
| 1                                                                                                     |   | <b>6a</b> | 87 <sup>[b]</sup>        |
| 2                                                                                                     |   | <b>6b</b> | 76                       |
| 3                                                                                                     |   | <b>6c</b> | 78                       |
| 4                                                                                                     |   | <b>6d</b> | 45 <sup>[b]</sup>        |
| 5                                                                                                     |   | <b>6e</b> | 55                       |
| 6                                                                                                     |   | <b>6f</b> | 42                       |

Typical conditions:  $HAuCl_4$  (4.50 mol %), **3** (9 mol %), aldehyde (1.00 mmol), alcohol (3.00 mmol), TBHP (1.50 mmol), 12 h. [a] Isolated yield. [b] Reaction required  $CH_3CN$  (1.00 mL) as solvent.

yields (Table 2, entries 4–6). Comparison with previously reported yields is only possible for **6a** (Table 2, entry 1). The palladium/phosphinous acid/PhSi(OMe)<sub>3</sub>/TBAF conditions were reported to deliver 92% yield, but required the use of expensive silane oxidant and 1 equiv of fluoride.<sup>[13]</sup>

For combinations of aliphatic aldehydes with previously tested alcohols (MeOH, *n*BuOH), the yields were comparable to the examples in which aromatic aldehydes were used. However, as a result of the low polarity of the esters generated from MeOH, we could only determine the yields by GC analysis. To alleviate problems with purification of the crude products, we used ethylene glycol as the alcohol component to generate polar products (Table 3). The lower

Table 3. Formation of 2-hydroxyethyl esters **7** from aliphatic aldehydes.

| Entry | R | Product   | Yield [%] <sup>[a]</sup> |
|-------|---|-----------|--------------------------|
| 1     |   | <b>7a</b> | 38                       |
| 2     |   | <b>7b</b> | 42                       |
| 3     |   | <b>7c</b> | 59                       |
| 4     |   | <b>7d</b> | 34                       |
| 5     |   | <b>7e</b> | 0                        |

Typical conditions: HAuCl<sub>4</sub> (4.50 mol %), **3** (9 mol %), aldehyde (1 mmol), alcohol (3.00 mmol), TBHP (1.50 mmol), CH<sub>3</sub>CN (1.00 mL), 12 h. [a] Isolated yield.

yields might be due, in part, to the application of a diol (see Table 2, entry 5). We have no evidence for the formation of the expected diesters derived from a two-fold reaction and the main by-product was, again, the acetal. Herein, the use of ethyleneglycol as the alcohol in these oxidative esterifications is described for the first time.

The proposed mechanism indicates initial Lewis acid activation of the aldehyde by the gold complex,<sup>[17]</sup> which leads to the formation of a hemiacetal by nucleophilic attack of the alcohol. The next step could be hydride transfer to the peroxide, which leads to the formation of the ester, *tert*-butanol and water. The formation of water could proceed through protonation of a preformed, unstable Au<sup>III</sup> hydroxide by the acidic pyridinium hydrochloride. The presence of pyridinium hydrochlorides was proven by the isolation of [AuCl<sub>4</sub>]<sup>−</sup>[PyH]<sup>+</sup> salt from a reaction mixture, after the reaction. The salt was characterised by X-ray crystallography (Figure 2).<sup>[18]</sup>

We could exclude radical-based reaction pathways, as well as Baeyer–Villiger-type oxidation, by the addition of radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the reaction mixture and by the use of 97% isotopically enriched <sup>18</sup>O-benzaldehyde.<sup>[19]</sup> After the reaction, 38% of the <sup>18</sup>O atoms were still incorporated. An exchange process by hy-

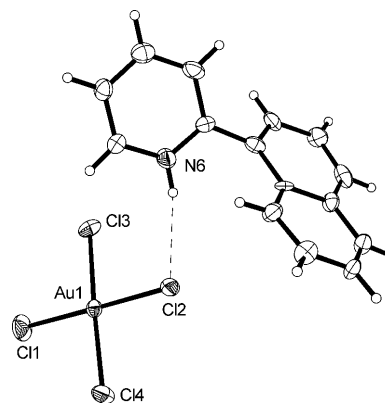


Figure 2. Crystal structure of [AuCl<sub>4</sub>]<sup>−</sup>[(1H)]<sup>+</sup>. With exception of the pyridinium proton all hydrogen atoms are omitted for clarity.

drate formation with unlabelled water that emerges from the catalytic reaction can explain the loss of isotopic purity.

With respect to the nature of the catalyst, we decided to use X-ray absorption spectroscopy (XAS) methodologies to prove the absence of nanoparticles as catalytic species. From X-ray absorption near-edge structure (XANES) and linear-combination XANES (LC-XANES) analysis information about the oxidation state of gold at the Au L<sub>III</sub> edge and the possible mixtures of different species with varying oxidation states can be obtained.<sup>[20]</sup> LC-XANES analysis on the spectra of HAuCl<sub>4</sub> (**VIII**) and AuCl (**IX**), as well as the reaction components **X–XIII**, was performed (see Tables 4 and 5). In the XANES spectrum of Au<sup>III</sup> (curve **IX**), a peak that is superimposed on the Au L<sub>III</sub> absorption edge was observed and is attributed to the Au 2p<sub>3/2</sub> → 5d transition.<sup>[21]</sup> The inten-

Table 4. Results from the LC-XANES fit in terms of weighting fraction of the reference spectra and compositions of the samples investigated.

|             | Weighting of HAuCl <sub>4</sub> /CH <sub>3</sub> CN ( <i>w</i> <sub>1</sub> ) | Weighting of AuCl (1− <i>w</i> <sub>1</sub> ) | Calculated Au–Cl average coordination number ( <i>N</i> ) <sup>[a]</sup> |
|-------------|-------------------------------------------------------------------------------|-----------------------------------------------|--------------------------------------------------------------------------|
| <b>VIII</b> | 1                                                                             | 0                                             | 4 (=NAu <sup>3+</sup> )                                                  |
| <b>IX</b>   | 0                                                                             | 1                                             | 2 (=NAu <sup>+</sup> )                                                   |
| <b>X</b>    | 0.951 ± 0.004                                                                 | 0.049 ± 0.004                                 | 3.90                                                                     |
| <b>XI</b>   | 0.934 ± 0.003                                                                 | 0.066 ± 0.003                                 | 3.87                                                                     |
| <b>XII</b>  | 0.882 ± 0.004                                                                 | 0.118 ± 0.004                                 | 3.76                                                                     |
| <b>XIII</b> | 0.144 ± 0.017                                                                 | 0.856 ± 0.017                                 | 2.29                                                                     |

[a]  $N = w_1 N(\text{Au}^{3+}) + (1 - w_1) N(\text{Au}^+)$ .

Table 5. Reaction conditions in accordance with the conditions outlined in the Experimental Section.

| Sample      | AuCl | HAuCl <sub>4</sub> | <b>3</b> | BA <sup>[a]</sup> | <i>n</i> -butanol | TBHP | <i>t</i> [h] |
|-------------|------|--------------------|----------|-------------------|-------------------|------|--------------|
| <b>VIII</b> |      | ○                  |          |                   |                   |      | 1            |
| <b>IX</b>   | ○    |                    |          |                   |                   |      | 1            |
| <b>X</b>    |      | ○                  | ○        |                   |                   |      | 1            |
| <b>XI</b>   |      | ○                  | ○        | ○                 | ○                 |      | 1            |
| <b>XII</b>  |      | ○                  | ○        | ○                 | ○                 | ○    | 1            |
| <b>XIII</b> |      | ○                  | ○        | ○                 | ○                 | ○    | 24           |

[a] BA = benzaldehyde.

sity of this peak is reduced in Au<sup>I</sup> (curve **VIII**) relative to Au<sup>III</sup> and is almost absent for Au<sup>0</sup>. In Figure 3, the Au L<sub>III</sub> edge XANES spectra of the reaction mixture after the addition of different reactants (curves **X–XIII**) are compared with the Au<sup>III</sup> and Au<sup>I</sup> reference spectra (curves **VIII** and

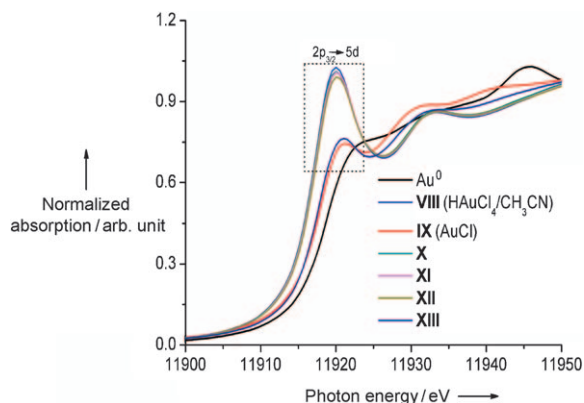


Figure 3. XANES spectra of Au<sup>0</sup> reference (gold metal foil) and of samples **VIII–XIII**.

**IX**). The spectra look similar to the Au<sup>III</sup> or Au<sup>I</sup> references but not to the Au<sup>0</sup> metal spectrum. The LC-XANES fits to the measured spectra are presented in the Supporting Information and the weighting factor of the two reference spectra necessary to obtain a reasonable fit are given in Table 4.

At any given point in time, the reaction mixture consists of an assortment of gold species, which coexist in solution. As a result of the limited analysis options at the cyclotron, we ensured that the reaction could be run under the predominant conditions. External parallel reactions with authentic aliquots of the reaction mixture converted whilst the different XAS spectra were measured. The reaction does not require absolute conditions and the use of technical-grade chemicals does not influence the reaction outcome. Use of the extended X-ray absorption fine structure (EXAFS) technique provides a structural picture that shows the average coordination around different Au centres (Table 4). The Fourier transform of the EXAFS function does not reveal the contribution of near neighbours either in gold-metal foil or in nanoparticles, which strongly indicates that no gold(0) participates in the catalytic cycle (Figure 4).<sup>[22]</sup> For all the investigated reaction mixtures EXAFS contribution is only observed from Au–Cl neighbours.

Nevertheless, catalyst deactivation does take place and sometimes arises from the formation of small gold particles, which showed no catalytic activity. Moreover, it was possible to isolate some Au<sup>I</sup> and Au<sup>III</sup> compounds after the reaction (Figures 2 and 5). Both [AuCl<sub>4</sub>]<sup>−</sup>[(1H)]<sup>+</sup> from Figure 1 and the gold(I) complex from Figure 5 are not active for oxidation. Thus, from these isolated species no evidence for the involvement or preference of certain oxidation states can be obtained. This is not surprising as the complexes were isolated after the reaction was completed, therefore, they origi-

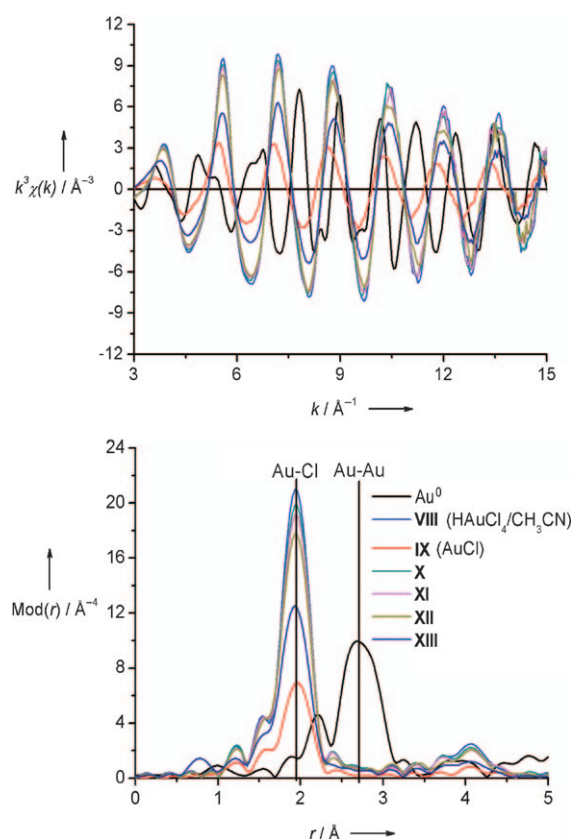


Figure 4. Experimental EXAFS spectra. Top:  $k^3$  weighted. Bottom: Fourier-transformed EXAFS spectra indicating the Au–Cl and Au–Au near-neighbour distances and the decrease in the intensity of the Au–Cl peak.

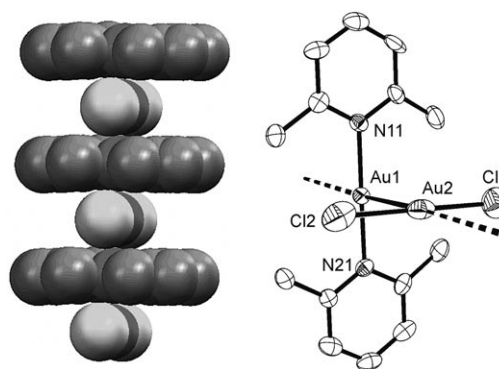


Figure 5. Crystal structure of a Au<sup>I</sup> compound isolated after the reaction. Hydrogen atoms are omitted for clarity. Left: top view of the space-filling presentation. Right: ellipsoid model.

nate from the decomposition of the active species and are not active themselves.

Figure 5 shows the solid-state structure of a linearly arranged Au<sup>I</sup> compound. In the solid state the [AuCl<sub>2</sub>]<sup>−</sup> units and the [Au(2,6-dimethylpyridine)]<sup>+</sup> units alternate. The distances between the counterions are 333.4 and 332.8 pm in turn and lie in the typical range for aurophilic interactions. In this catalysis reaction, 2,6-dimethylpyridine was used as stabilising agent. In addition to this, we synthesised gold(III)

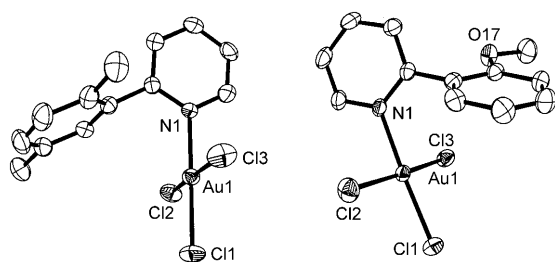


Figure 6. Solid-state structures of  $[\text{AuCl}_3\cdot\mathbf{3}]$  (right) and  $[\text{AuCl}_3\cdot\mathbf{4}]$  (left). Hydrogen atoms are omitted for clarity.

complexes with pyridines **1–4** as ligands. Figure 6 presents the solid-state structures of  $[\text{AuCl}_3\cdot\mathbf{3}]$  and  $[\text{AuCl}_3\cdot\mathbf{4}]$ . These structures show that the stabilising effect might arise from coordination of the pyridine to the gold centre during the reaction. The Au–N distances are 204.4 and 203.9 pm for  $[\text{AuCl}_3\cdot\mathbf{3}]$  and  $[\text{AuCl}_3\cdot\mathbf{4}]$ , respectively. A more detailed study of these and other  $\text{Au}^{\text{III}}$  complexes, as well as a study of their catalytic activity in other reactions, is under examination.

## Conclusion

We have provided the first experimental proof that, in addition to the known oxidation reactions with gold nanoparticles, mononuclear gold complexes can also be active catalysts in oxidation reactions. The selective oxidative esterification of aldehydes and alcohols also opens interesting further synthetic perspectives.

## Experimental Section

**General methods:** All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma–Aldrich or VWR and were used without further purification, unless otherwise noted. Deuterated solvents were purchased from Euriso–Top. Solvents were dried by using a MB SPS-800 solvent purification system with the aid of drying columns. Preparation of air- and moisture-sensitive materials was carried out by using Schlenk techniques in flame-dried flasks under an atmosphere of nitrogen. Oxidation reactions were performed in dry and degassed solvents. TLC was performed by using Polygram precoated plastic sheets SIL G/UV<sub>254</sub> ( $\text{SiO}_2$ , 0.20 mm thickness) from Macherey–Nagel. Column chromatography was performed on silica gel (40.0–63.0 nm particle size) from Macherey–Nagel. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers at RT. Chemical shifts ( $\delta$ , ppm) were referenced to TMS.<sup>[23]</sup> Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).  $^{13}\text{C}$  assignment was achieved with the aid of DEPT90 and DEPT135 spectra. MS spectra were recorded on Vakkum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometers. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer.

**Compounds 1–4:** Compounds **1–4** were synthesised according to literature procedures.<sup>[24–27]</sup>

**General procedure for the synthesis of esters 5–7:** Under an atmosphere of argon,  $\text{HAuCl}_4\cdot x\text{H}_2\text{O}$  (49% metal content) (17.7 mg, 45.0  $\mu\text{mol}$ ) was mixed with **3** (16.6 mg, 90.0  $\mu\text{mol}$ ) and acetonitrile (1.00 mL) to give a dark-orange solid. Alcohol (3.00 mmol), aldehyde (1.00 mmol) and TBHP (5.50 M in decane, 270  $\mu\text{L}$ , 1.50 mmol) were added to the reaction

mixture sequentially. The mixture was stirred for 12 h at 75°C, the solvent was removed under reduced pressure and the products were purified by silica-gel column chromatography (petroleum ether (PE)/ethyl acetate (EA)). Experiments **I–VII** were carried out in a comparable manner.

**Butyl benzoate (5a):** Column chromatography (PE/EA 100:0→15:1); colourless oil; yield: 160 mg, 900  $\mu\text{mol}$ , 90%;  $R_f$  (PE/EA 15:1)=0.49;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.96 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.46 (m,  $J(\text{H,H})$ =7.6 Hz, 2H;  $\text{CH}_2$ ), 1.73 (m,  $J(\text{H,H})$ =6.9 Hz, 2H;  $\text{CH}_2$ ), 4.31 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 7.41 (t,  $J(\text{H,H})$ =7.7 Hz, 2H; ArH), 7.52 (t,  $J(\text{H,H})$ =7.4 Hz, 2H; ArH), 8.03 ppm (d,  $J(\text{H,H})$ =8.2 Hz, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.92, 19.45, 30.96, 64.99, 128.32, 128.45, 130.72, 129.93, 168.83 ppm. All data are in good agreement with commercially available **5a**.

**Butyl 4-methylbenzoate (5b):** Column chromatography (PE/EA 100:0→15:1); colourless oil; yield: 142 mg, 740  $\mu\text{mol}$ , 74%;  $R_f$  (PE/EA 15:1)=0.49;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.96 (t,  $J(\text{H,H})$ =7.5 Hz, 3H;  $\text{CH}_3$ ), 1.45 (m, 2H;  $\text{CH}_2$ ), 1.72 (m, 2H;  $\text{CH}_2$ ), 2.38 (s, 3H;  $\text{CH}_3$ ), 4.29 (t,  $J(\text{H,H})$ =6.6 Hz, 2H;  $\text{CH}_2$ ), 7.21 (d,  $J(\text{H,H})$ =8.1 Hz, 2H; ArH), 7.91 ppm (d,  $J(\text{H,H})$ =8.1 Hz, 2H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.96, 19.50, 21.84, 31.02, 64.85, 128.02, 129.22, 129.76, 143.60, 166.98 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[28]</sup>

**Butyl 2,4,6-trimethylbenzoate (5c):** Purification by bulb-to-bulb distillation; colourless oil; yield: 172 mg, 780  $\mu\text{mol}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.95 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.44 (m, 2H;  $\text{CH}_2$ ), 1.72 (m, 2H;  $\text{CH}_2$ ), 2.27 (s, 3H;  $\text{CH}_3$ ), 2.29 (s, 6H;  $\text{CH}_3$ ), 4.31 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 6.64 ppm (s, 2H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.86, 19.47, 19.89, 21.27, 30.89, 64.89, 128.53, 135.14, 139.29, 170.47 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[29]</sup>

**Butyl 2-naphthoate (5d):** Column chromatography (PE/EA 15:1); colourless solid; yield: 164 mg, 720  $\mu\text{mol}$ , 72%;  $R_f$  (PE/EA 15:1)=0.33;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.91 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.43 (m, 2H;  $\text{CH}_2$ ), 1.71 (m, 2H;  $\text{CH}_2$ ), 4.30 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 7.45 (m, 2H; ArH), 7.77 (dd,  $J(\text{H,H})$ =8.6, 2.1 Hz, 2H; ArH), 7.85 (d,  $J(\text{H,H})$ =7.9 Hz, 1H; ArH), 7.97 (dd,  $J$ =8.6, 1.7 Hz, 1H; ArH), 8.51 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.97, 19.50, 31.03, 65.16, 125.43, 126.74, 127.91, 127.96, 128.25, 128.30, 129.45, 131.09, 132.68, 135.65, 166.99 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[30]</sup>

**Butyl 4-methoxybenzoate (5e):** Column chromatography (PE/EA 15:1); colourless oil; yield: 141 mg, 680  $\mu\text{mol}$ , 68%;  $R_f$  (PE/EA 15:1)=0.25;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.96 (t,  $J(\text{H,H})$ =7.5 Hz, 3H;  $\text{CH}_3$ ), 1.45 (m, 2H;  $\text{CH}_2$ ), 1.72 (m, 2H;  $\text{CH}_2$ ), 2.38 (s, 3H;  $\text{CH}_3$ ), 4.29 (t,  $J(\text{H,H})$ =6.6 Hz, 2H;  $\text{CH}_2$ ), 7.21 (d,  $J(\text{H,H})$ =8.1 Hz, 2H; ArH), 7.91 ppm (d,  $J(\text{H,H})$ =8.1 Hz, 2H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.96, 19.50, 21.84, 31.02, 64.85, 128.02, 129.22, 129.76, 143.60, 166.98 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[31]</sup>

**Butyl 2-bromo-4,5-dimethoxybenzoate (5f):** Column chromatography (PE/EA/ $\text{CH}_2\text{Cl}_2$  7:1:1); colourless solid; yield: 141 mg, 320  $\mu\text{mol}$ , 32%;  $R_f$  (PE/EA/ $\text{CH}_2\text{Cl}_2$  7:1:1)=0.31;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.94 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.46 (m, 2H;  $\text{CH}_2$ ), 1.73 (m, 2H;  $\text{CH}_2$ ), 2.38 (s, 3H;  $\text{CH}_3$ ), 3.86 (s, 3H;  $\text{CH}_3$ ), 3.88 (s, 3H;  $\text{CH}_3$ ), 4.29 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 7.01 (s, 1H; ArH), 7.37 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.94, 19.52, 28.34, 30.86, 56.30, 56.45, 114.10, 114.22, 117.10, 123.65, 147.99, 152.08, 165.84 ppm; HRMS (EI<sup>+</sup>):  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{17}\text{BrO}_4$ : 316.0310 [ $M$ ]<sup>+</sup>; found: 316.0303.

**Butyl 4-nitrobenzoate (5g):** Column chromatography (PE/EA 15:1); colourless solid; yield: 107 mg, 480  $\mu\text{mol}$ , 48%;  $R_f$  (PE/EA 15:1)=0.38;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.97 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.46 (m, 2H;  $\text{CH}_2$ ), 1.76 (m, 2H;  $\text{CH}_2$ ), 4.36 (t,  $J(\text{H,H})$ =6.6 Hz, 2H;  $\text{CH}_2$ ), 8.18 (m, 2H; ArH), 8.26 ppm (m, 2H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.94, 19.45, 30.87, 66.03, 123.72, 136.10, 150.70, 164.95 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[32]</sup>

**Butyl-3-chlorobenzoate (5h):** Column chromatography (PE/EA 15:1); colourless oil; yield: 127 mg, 600  $\mu\text{mol}$ , 60%;  $R_f$  (PE/EA 15:1)=0.49;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.02 (t,  $J(\text{H,H})$ =7.3 Hz, 3H;  $\text{CH}_3$ ), 1.51 (m, 2H;  $\text{CH}_2$ ), 1.79 (m, 2H;  $\text{CH}_2$ ), 4.36 (t,  $J(\text{H,H})$ =6.6 Hz, 2H;  $\text{CH}_2$ ), 7.52 (m, 3H; ArH), 8.08 ppm (d,  $J(\text{H,H})$ =7.3 Hz, 2H; ArH). Product could not be isolated in pure form; determination of the yield was accomplished by  $^1\text{H}$  NMR signal integration. All data is in good agreement with data for commercially available **5h**.

**(E)-Butyl cinnamate (5i):** Column chromatography (PE/EA 15:1); colourless oil; yield: 96 mg, 470  $\mu\text{mol}$ , 47%;  $R_f$  (PE/EA 15:1)=0.55;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.95 (t,  $J(\text{H,H})$ =7.3 Hz, 3H;  $\text{CH}_3$ ), 1.42 (m, 2H;  $\text{CH}_2$ ), 1.73 (m, 2H;  $\text{CH}_2$ ), 4.19 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 6.42 (d,  $J(\text{H,H})$ =16 Hz, 1H; =CH), 7.36 (m, 3H; ArH), 7.51 (m, 2H; ArH), 7.67 ppm (d,  $J(\text{H,H})$ =16.0 Hz, 1H; =CH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.95, 19.40, 30.98, 64.63, 118.49, 128.23, 129.05, 130.39, 134.66, 144.74, 167.29 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[33]</sup>

**Methyl 2-naphthoate (6a):** Column chromatography (PE/EA 15:1); colourless solid; yield: 166 mg, 830  $\mu\text{mol}$ , 83%;  $R_f$  (PE/EA 15:1)=0.49;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =3.97 (s, 3H,  $\text{CH}_3$ ), 7.56 (m, 2H; ArH), 7.86 (d,  $J(\text{H,H})$ =9.0 Hz, 2H), 7.94 (dd,  $J$ =7.8, 1.7 Hz, 1H; ArH), 8.05 (dd,  $J(\text{H,H})$ =8.6, 1.7 Hz, 1H; ArH), 8.60 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =52.45, 125.42, 126.84, 127.58, 127.96, 128.35, 128.43, 129.55, 131.26, 132.68, 135.70, 167.47 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[13]</sup>

**Ethyl 2-naphthoate (6b):** Column chromatography (PE/EA 15:1); colourless solid; yield: 128 mg, 640  $\mu\text{mol}$ , 64%;  $R_f$  (PE/EA 15:1)=0.43;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.44 (t,  $J(\text{H,H})$ =7.2 Hz, 3H;  $\text{CH}_3$ ), 4.44 (q,  $J(\text{H,H})$ =7.2 Hz, 2H;  $\text{CH}_2$ ), 7.56 (m, 2H; ArH), 7.86 (d,  $J(\text{H,H})$ =9.0 Hz, 2H; ArH), 7.94 (dd,  $J(\text{H,H})$ =7.8, 1.7 Hz, 1H; ArH), 8.05 (dd,  $J(\text{H,H})$ =8.6, 1.7 Hz, 1H; ArH), 8.61 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =14.60, 61.28, 125.45, 126.76, 127.94, 128.26, 128.32, 129.51, 131.22, 132.70, 135.67, 166.95 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[34]</sup>

**Octyl 2-naphthoate (6c):** Column chromatography (PE/EA 15:1); colourless solid; yield: 208 mg, 730  $\mu\text{mol}$ , 73%;  $R_f$  (PE/EA 15:1)=0.71;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.88 (t,  $J(\text{H,H})$ =6.8 Hz, 3H;  $\text{CH}_3$ ), 1.24–1.49 (m, 10H;  $5 \times \text{CH}_2$ ), 1.81 (m, 2H;  $\text{CH}_2$ ), 4.37 (t,  $J(\text{H,H})$ =6.7 Hz, 2H;  $\text{CH}_2$ ), 7.55 (m, 2H; ArH), 7.86 (d,  $J(\text{H,H})$ =8.7 Hz, 2H; ArH), 7.94 (d,  $J(\text{H,H})$ =7.7 Hz, 1H; ArH), 8.05 (dd,  $J(\text{H,H})$ =8.6, 1.8 Hz, 1H; ArH), 8.59 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =14.31, 22.87, 26.31, 29.01, 29.43, 29.51, 32.03, 65.53, 125.48, 126.78, 127.96, 128.02, 128.29, 128.34, 129.54, 131.13, 132.73, 135.69, 167.04 ppm; IR (KBr):  $\tilde{\nu}$ =2954, 2931, 2855, 1718, 1468, 1390, 1354, 1285, 1228, 1196, 1154, 1131, 1097, 1016, 959, 913, 866, 828, 780, 763  $\text{cm}^{-1}$ ; HRMS ( $\text{EI}^+$ ):  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_2$ : 284.1776  $[M]^+$ ; found: 284.1835.

**sec-Butyl 2-naphthoate (6d):** Column chromatography (PE/EA 15:1); colourless solid; yield: 95.9 mg, 420  $\mu\text{mol}$ , 42%;  $R_f$  (PE/EA 15:1)=0.68;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.00 (t,  $J(\text{H,H})$ =7.5 Hz, 3H;  $\text{CH}_3$ ), 1.38 (d,  $J(\text{H,H})$ =6.3 Hz, 3H;  $\text{CH}_3$ ), 1.75 (m, 2H;  $\text{CH}_2$ ), 5.16 (m, 1H; CH), 7.55 (m, 2H; ArH), 7.86 (d,  $J(\text{H,H})$ =8.6 Hz, 2H; ArH), 7.96 (dd,  $J(\text{H,H})$ =7.6, 1.8 Hz, 1H; ArH), 8.05 (dd,  $J(\text{H,H})$ =8.6, 1.6 Hz, 1H; ArH), 8.59 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =10.02, 19.85, 29.25, 73.23, 125.52, 126.75, 127.94, 128.24, 128.28, 128.40, 129.52, 131.02, 132.73, 135.66, 166.60 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[35]</sup>

**2-Hydroxyethyl 2-naphthoate (6e):** Column chromatography (PE/EA 4:1); colourless solid; yield: 119 mg, 550  $\mu\text{mol}$ , 55%;  $R_f$  (PE/EA 4:1)=0.17;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =2.43 (s, 1H; OH), 3.99 (m, 2H;  $\text{CH}_2$ ), 4.52 (m, 2H;  $\text{CH}_2$ ), 7.55 (m, 2H; ArH), 7.86 (d,  $J(\text{H,H})$ =8.6 Hz, 2H; ArH), 7.93 (dd,  $J(\text{H,H})$ =7.9, 1.6 Hz, 1H; ArH), 8.05 (dd,  $J(\text{H,H})$ =8.6, 1.6 Hz, 1H; ArH), 8.61 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =61.72, 67.03, 125.40, 126.93, 127.27, 127.99, 128.44, 128.59, 129.57, 131.48, 132.65, 135.83, 167.34 ppm. All

spectroscopic data are in good agreement with the previously reported data.<sup>[36]</sup>

**Cyclohexyl 2-naphthoate (6f):** Column chromatography (PE/EA 15:1); colourless solid; yield: 107 mg, 420  $\mu\text{mol}$ , 42%;  $R_f$  (PE/EA 15:1)=0.38;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.24–1.69 (m, 6H;  $\text{CH}_2$ ), 1.78 (m, 2H;  $\text{CH}_2$ ), 1.96 (m, 2H;  $\text{CH}_2$ ), 5.05 (tt,  $J(\text{H,H})$ =8.9, 3.8 Hz, 1H; CH), 7.51 (m, 2H; ArH), 7.82 (d,  $J(\text{H,H})$ =8.4 Hz, 2H; ArH), 7.91 (m, 1H; ArH), 8.03 (dd,  $J(\text{H,H})$ =8.6, 1.7 Hz, 1H; ArH), 8.56 ppm (s, 1H; ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =23.96, 25.73, 31.94, 73.45, 125.53, 126.73, 127.93, 128.21, 128.25, 128.49, 129.52, 131.04, 132.72, 135.65, 166.34 ppm; IR (KBr):  $\tilde{\nu}$ =3058, 2939, 2853, 1715, 1631, 1455, 1357, 1320, 1282, 1262, 1234, 1200, 1134, 1106, 1095, 1016, 962, 782, 762  $\text{cm}^{-1}$ ; HRMS ( $\text{EI}^+$ ):  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : 254.1307  $[M]^+$ ; found: 254.1346.

**2-Hydroxyethyl isobutyrate (7a):** Column chromatography (PE/EA 2:1); colourless oil; yield: 50.2 mg, 380  $\mu\text{mol}$ , 38%;  $R_f$  (PE/EA 2:1)=0.28;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.15 (d,  $J(\text{H,H})$ =7.0 Hz, 6H;  $\text{CH}_3$ ), 2.56 (septet,  $J(\text{H,H})$ =7.0 Hz, 1H; CH), 3.79 (m, 2H;  $\text{CH}_2$ ), 4.17 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =19.16, 34.12, 61.49, 66.14, 177.77 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[37]</sup>

**2-Hydroxyethyl pivalate (7b):** Column chromatography (PE/EA 2:1); colourless oil; yield: 62.9 mg, 420  $\mu\text{mol}$ , 42%;  $R_f$  (PE/EA 2:1)=0.29;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =1.20 (s, 9H;  $\text{CH}_3$ ), 2.10 (s, 1H; OH), 3.80 (m, 2H;  $\text{CH}_2$ ), 4.18 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =27.39, 39.04, 61.67, 66.31, 179.21 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[38]</sup>

**2-Hydroxyethyl butanoate (7c):** Column chromatography (PE/EA 2:1); colourless oil; yield: 60.0 mg, 450  $\mu\text{mol}$ , 45%;  $R_f$  (PE/EA 2:1)=0.18;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.92 (t,  $J(\text{H,H})$ =7.4 Hz, 3H;  $\text{CH}_3$ ), 1.64 (m, 2H;  $\text{CH}_2$ ), 1.61 (m, 2H;  $\text{CH}_2$ ), 2.32 (t,  $J(\text{H,H})$ =7.4 Hz, 2H;  $\text{CH}_2$ ; overlapping with 1H; OH), 3.79 (m, 2H;  $\text{CH}_2$ ), 4.18 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =13.83, 18.60, 36.23, 61.46, 66.06, 174.28 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[39]</sup>

**2-Hydroxyethyl hexanoate (7d):** Column chromatography (PE/EA 2:1); colourless oil; yield: 54.5 mg, 340  $\mu\text{mol}$ , 34%;  $R_f$  (PE/EA 2:1)=0.16;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =0.78 (t,  $J(\text{H,H})$ =6.9 Hz, 3H;  $\text{CH}_3$ ), 1.28 (m, 4H;  $\text{CH}_2$ ), 1.61 (m, 2H;  $\text{CH}_2$ ), 2.32 (m, 2H;  $\text{CH}_2$ ; overlapping with 1H; OH), 3.71 (m, 2H;  $\text{CH}_2$ ), 4.18 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25°C, TMS):  $\delta$ =14.09, 22.50, 24.80, 31.48, 34.36, 61.48, 66.10 ppm. All spectroscopic data are in good agreement with the previously reported data.<sup>[40]</sup>

## Acknowledgements

The authors would like to express their special thanks to the Deutsche Forschungsgemeinschaft (DFG Sonderforschungsbereich SFB 706) as well as to the Studienstiftung des Dt. Volkes e.V. (fellowship for C.L.).

- [1] For representative reviews on gold catalysis, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) A. Fürstner, P. W. Davis, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; c) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; d) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; e) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; f) Z. G. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265.
- [2] a) B. Guan, D. Xing; B. Guan, G. Cai, Z. Fang, L. Yang, Z. Shi, *Org. Lett.* **2006**, *8*, 693–696; G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, *J. Am. Chem. Soc.* **2005**, *127*, 18004–18005; b) H. Li, B. Guan, W. Wang, D. Xing, Z. Fang, X. Wan, L. Yang, Z. Shi, *Tetrahedron* **2007**, *63*, 8430–8434.

- [3] D. Xing; B. Guan, G. Cai, Z. Fang, L. Yang, Z. Shi, *Org. Lett.* **2006**, 8, 693–696.
- [4] Y. Yuan, Y. Bian, *Tetrahedron Lett.* **2007**, 48, 8518–8520.
- [5] a) G. M. Smith, *J. Am. Chem. Soc.* **1922**, 44, 1769–1775; b) G. Natile, E. Bordignon, L. Cattalini, *Inorg. Chem.* **1976**, 15, 246–248; c) G. Annibale, L. Canovese, L. Cattalini, G. Natile, *J. Chem. Soc. Dalton Trans.* **1980**, 1017–1021.
- [6] E. Boring, Y. Geletii, C. L. Hill, *J. Am. Chem. Soc.* **2001**, 123, 1625–1635.
- [7] a) A. Kar, N. Mangu, H. M. Kaiser, M. Beller, M. K. Tse, *Chem. Commun.* **2008**, 386–388; b) H. A. Wegner, S. Ahles, M. Neuburger, *Chem. Eur. J.* **2008**, 14, 11310–11313; c) L. Cui, G. Zhang, L. Zhang, *Bioorg. Med. Chem. Lett.* **2009**, 19, 3884–3887; d) G. Zhang, Y. Peng, L. Cui, L. Zhang, *Angew. Chem.* **2009**, 121, 3158–3161; *Angew. Chem. Int. Ed.* **2009**, 48, 3112–3115.
- [8] a) M. Haruta, *Chem. Rec.* **2003**, 3, 75–87; b) D. I. Enache, D. W. Knight, G. J. Hutchings, *Catal. Lett.* **2005**, 103, 43–52; c) L. Prati, M. Rossi, *J. Catal.* **1998**, 176, 552–560; d) F. Porta, L. Prati, M. Rossi, S. Colluccia, G. Martra, *Catal. Today* **2000**, 61, 165–172; e) C. Bianchi, F. Porta, L. Prati, M. Rossi, *Top. Catal.* **2000**, 13, 231–236; f) L. Prati, *Gold Bull.* **1999**, 32, 96–101; g) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G. J. Hutchings, *Chem. Commun.* **2002**, 696–698; h) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2003**, 5, 1329–1336; i) N. Dimitratos, F. Porta, L. Prati, A. Villa, *Catal. Lett.* **2005**, 99, 181–185; j) M. Benson, P. Gallezot, *Catal. Today* **2000**, 57, 127–141; k) for a representative review, see: C. Della Pina, E. Falletta, L. Prati, M. Rossi, *Chem. Soc. Rev.* **2008**, 37, 2077–2095.
- [9] a) I. S. Nielsen, E. Taarning, K. Egeblad, R. Madsen, C. H. Christensen, *Catal. Lett.* **2007**, 116, 35–40; b) A. Abad, C. Amela, A. Corma, H. Garcia, *Tetrahedron* **2006**, 62, 6666–6672; c) S. Biella, L. Prati, M. Rossi, *J. Mol. Catal. A* **2003**, 197, 207–212.
- [10] R. Gopinath, B. K. Patel, *Org. Lett.* **2000**, 2, 577–579.
- [11] W.-J. Yoo, C.-J. Li, *Tetrahedron Lett.* **2007**, 48, 1033–1035.
- [12] B. R. Travis, M. Sivakumar, G. O. Hollist, B. Borhan, *Org. Lett.* **2003**, 5, 1031–1034.
- [13] R. Lerebours, C. Wolf, *J. Am. Chem. Soc.* **2006**, 128, 13052–13053.
- [14] P. Fristrup, L. B. Johansen, C. H. Christensen, *Chem. Commun.* **2008**, 2750–2752.
- [15] a) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, 311, 362–365; b) A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, 117, 4134–4137; *Angew. Chem. Int. Ed.* **2005**, 44, 4066–4069.
- [16] a) A. Caupy, M. Pedoussant, J. Sansoulet, *J. Org. Chem.* **1986**, 51, 740–742; b) H. Sharghi, M. H. Savari, R. Eskandari, *J. Chem. Res.* **2005**, 488–491.
- [17] V. Nair, K. G. Abhilash, N. Vidya, *Org. Lett.* **2005**, 7, 5857–5859.
- [18] CCDC-758174 ([AuCl<sub>2</sub>]<sup>−</sup>[Au(2,6-dimethylpyridine)]<sup>+</sup>), 758175 ([AuCl<sub>3</sub>·(4)]), 758176 ([AuCl<sub>4</sub>]<sup>−</sup>[PyH]<sup>+</sup>) and 758177 ([AuCl<sub>3</sub>·(3)])
- contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [19] P. H. J. Carlsen, M. Ystenes, *Acta Chem. Scand. B* **1986**, 40, 757–759.
- [20] C. Lamberti, S. Bordiga, F. Bonino, C. Prestipino, G. Berlier, L. Capello, F. D'Acapito, F. X. Llabrés i Xamena, A. Zecchina, *Phys. Chem. Chem. Phys.* **2003**, 5, 4502–4509.
- [21] a) J.-H. Choy, Y.-I. Kim, *J. Phys. Chem. B* **2003**, 107, 3348–3350; b) A. Pantelouris, G. Küper, J. Homes, C. Feldmann, M. Jansen, *J. Am. Chem. Soc.* **1995**, 117, 11749–11753.
- [22] Y. Sun, A. I. Frenkel, H. White, L. Zhang, Y. Zhu, H. Xu, J. C. Yang, T. Koga, V. Zaitsev, M. H. Rafailovich, J. C. Sokolov, *J. Phys. Chem. B* **2006**, 110, 23022–23030.
- [23] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, 62, 7512–7515.
- [24] C. M. So, C. C. Yeung, C. P. Lau, F. Y. Kwong, *J. Org. Chem.* **2008**, 73, 7803–7806.
- [25] T. J. Colacot, W. A. Carole, B. A. Neide, A. Harad, *Organometallics* **2008**, 27, 5605–5611.
- [26] O. Lohse, P. Thevenin, E. Waldvogel, *Synlett* **1999**, 45–48.
- [27] K. L. Billingsley, S. L. Buchwald, *Angew. Chem.* **2008**, 120, 4773–4776; *Angew. Chem. Int. Ed.* **2008**, 47, 4695–4698.
- [28] J. McNulty, J. J. Nair, A. Robertson, *Org. Lett.* **2007**, 9, 4575–4578.
- [29] A. Loupy, M. Pedoussaut, J. Sansoulet, *J. Org. Chem.* **1986**, 51, 740–742.
- [30] B. E. Maki, A. Chan, E. M. Phillips, K. A. Scheidt, *Org. Lett.* **2007**, 9, 371–374.
- [31] H. Neumann, A. Brennfuehrer, P. Gross, T. Riermeier, J. Almena, M. Beller, *Adv. Synth. Catal.* **2006**, 348, 1255–1261.
- [32] T. Iwasaki, Y. Maegawa, Y. Hayashi, T. Ohshima, K. Mashima, *J. Org. Chem.* **2008**, 73, 5147–5150.
- [33] T. Fukuyama, M. Arai, H. Matsubara, I. Ryu, *J. Org. Chem.* **2004**, 69, 8105–8107.
- [34] A. Palmelund, E. L. Myers, L. R. Tai, S. Tisserand, C. P. Butts, V. K. Aggarwal, *Chem. Commun.* **2007**, 4128–4130.
- [35] J. Kenyon, R. H. Pickard, *J. Chem. Soc.* **1915**, 115–132.
- [36] H. Sharghi, M. H. Sarvari, M. A. Moni, *Tetrahedron* **2003**, 59, 3627–3633.
- [37] Y. Imada, H. Iida, T. Naota, *J. Am. Chem. Soc.* **2005**, 127, 14544–14545.
- [38] P. Prabhakar, N. Suryakiran, Y. Venkateswarlu, *Chem. Lett.* **2007**, 36, 732–733.
- [39] M. P. Hartshorn, D. N. Kirk, *Tetrahedron* **1966**, 22, 1415–1420.
- [40] B. Karimi, J. Rajabi, *J. Mol. Catal. A* **2005**, 226, 165–169.

Received: December 16, 2009

Revised: April 22, 2010

Published online: July 2, 2010