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A pentanuclear yttrium hydroxo cluster as an oxidation catalyst. Catalytic oxidation of aldehydes in the presence of air

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Received (in Cambridge, UK) 24th November 2003, Accepted 28th January 2004
First published as an Advance Article on the web 23rd February 2004

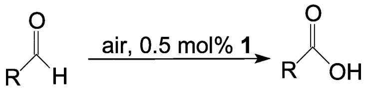
The air- and moisture-stable pentanuclear yttrium cluster $H_5[Y_5(\mu_4\text{-}O)(\mu_3\text{-}O)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6]$ (Ph_2acac = dibenzoylmethanide) has been used as a homogenous catalyst for the oxidation of aldehydes to the corresponding carboxylic acids in the presence of air.

In recent years, lanthanide clusters have attracted increasing interest[1] as a result of their novel structural characteristics and fascinating properties, as well as their many potential applications in fields such as in magnetic and optical materials and catalytic processes, and their use as precursors for lanthanide-based oxide materials.[2] The chemistry of lanthanide clusters is not as developed as the cluster chemistry of the transition metals.[3,4] This is particularly surprising given that oligomeric lanthanide structures are proposed to play a key role in some catalytic transformations.[5,6] Therefore, we set out to synthesise an easily accessible air-stable lanthanide cluster in order to investigate its properties in homogenous catalysis. It is well known that the most stable lanthanide clusters are oxo/hydroxo clusters. Recently, we and others have synthesised new tetradeca- and pentadecanuclear lanthanide oxo/hydroxo clusters.[7,8] Basically, two different approaches towards the preparation of oxo/hydroxo clusters were investigated. One way to obtain these compounds is the hydrolysis of a moisture-sensitive starting material, whereas the other approach is hydrolytic, wherein the water molecules are deprotonated in a controlled manner.[3,5] Most of the oxo/hydroxo clusters are stabilised by ligands such as alkoxides,[9] phenoxides,[5] β-diketones[10,11] and amino acids.[3] In contrast to the well-established solid-state structures of lanthanide oxo/hydroxo clusters, almost nothing is known about their potential in catalysis. In this paper, we report the synthesis and structural characterisation of an air- and moisture-stable pentanuclear yttrium cluster, $H_5[Y_5(\mu_4\text{-}O)(\mu_3\text{-}O)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4(\eta^2\text{-}Ph_2acac)_6]$ (**1**; Ph_2acac = dibenzoylmethanide), and its application in homogenous catalysis.

In order to have easy access to reasonable amounts of the proposed cluster catalyst, we followed a synthetic route which is comparable to a procedure described previously.[12,13] Reaction of one equivalent of $YCl_3 \cdot 6H_2O$ with two equivalents dibenzoylmethane in presence of triethylamine yields **1** as yellow crystals (eqn. 1).† Cluster **1** crystallises in the tetragonal space group *P*4/*n*,‡ the unit cell contains two discrete pentayttrium cores (Fig. 1) in a square-based pyramidal arrangement. This structure is similar to that of $[Eu_5(OH)_5(Ph_2acac)_{10}]$.[13] Each triangular face of the square pyramid is capped by one μ_3-O moiety, similar to $[Y_9O_2(OH)_8(aacac)_{16}]^-$ (aacac = allylacetoacetate),[10] $[Ln_9O_2(OH)_8(BA)_{16}]^-$ (BA = benzoylacetone, Ln = Sm, Eu, Gd, Dy, Er),[12] $[Ln_{14}(OH)_{18}(o\text{-}O_2NC_6H_4O)_{24}]$[7] (Ln = Er, Yb) and related compounds.[11,13] In the square-base face, four yttrium atoms are linked by one μ_4-O atom. In **1**, each yttrium ion is coordinated to eight oxygen atoms displaying a square antiprismatic arrangement. The Y_5 core is surrounded by ten peripheral ligands. The ligand shows two types of coordination behaviour. Six ligands are terminal chelates and four are bridging chelates bonding to two metal ions that belong to the base of the polyhedra. The apical yttrium, which lies on a fourfold symmetry axis, is bonded to two chelate ligands, which are disordered in the solid-state structure. The disorder in the structure may also be a result of a twinning problem. The formation of the hydroxy bridges can be explained by a closer look at the starting material. $YCl_3 \cdot 6H_2O$ is, in fact, an ionic species of composition $[Y(H_2O)_6Cl_2]^+Cl^-$ in which the six water molecules are coordinated *via* the oxygen atom onto the metal centre. Addition of base just leads to deprotonation of the coordinated water molecules. The pentanuclear arrangement of **1** is a common structural motif for lanthanide oxo/hydroxo clusters.[10,13,14] We chose this common structural motif so that we would have easy access to nanostructural lanthanide catalysts.

$$5\left[YCl_2\left(H_2O\right)_6\right]^+Cl^- + 10\,Ph_2acacH \xrightarrow[\substack{-15\,HNEt_3Cl\\ -25\,H_2O}]{15\,NEt_3} H_5\left[Y_5O_5\left(Ph_2acac\right)_{10}\right] \quad (1)$$

Our intention was to use **1** as catalyst for an aldol reaction. Therefore, cyclohexylcarbaldehyde, acetone, small amounts of water and catalytic amounts (0.5 mol%) of **1** were mixed together in CH_2Cl_2. To our surprise, no aldol condensation product was formed. Instead, the aldehyde was oxidised quantitatively to the corresponding carboxylic acid. Under these conditions, the reaction was complete after 12 h. No isopropanol byproduct was detected by GC/MS. Later, it turned out that the reaction also runs without acetone and water. However, when leaving out **1** or performing the reaction under a nitrogen atmosphere, no oxidation reaction was observed. Therefore, we propose that the aldehyde is oxidised by oxygen from the air (eqn. 2).§ Besides the carboxylic acid, traces of cyclohexanol and cyclohexanone were also detected by GC/MS. It was established previously that air oxidation of aliphatic aldehydes leads to these byproducts *via* CO extrusion.[15]



(2)

In the next step, the scope and the limitations of the reaction were investigated. A variety of aliphatic, olefinic and aromatic aldehydes were used as starting materials (Table 1). It turned out that aliphatic aldehydes are converted in high yields under the conditions described above (entry 1–4). Thus, turnover numbers up to 200 have been achieved in 12 h. On the other hand, aromatic systems are not oxidised (entry 7 and 8). A C=C double bond has a negative

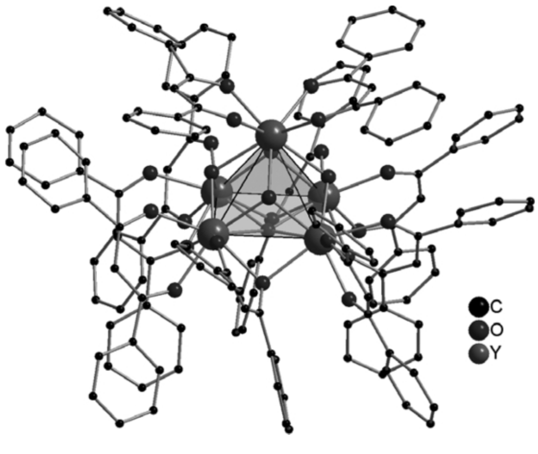
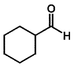
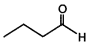
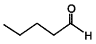
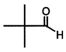
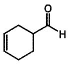
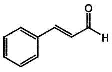
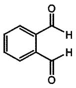
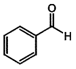


Fig. 1 Solid-state structure of **1**, with hydrogen atoms omitted.

DOI: 10.1039/b315218a

Table 1 Air oxidation of aldehydes catalysed by **1**[a]

Entry	Aldehyde	Reaction time/h	Yield[b] (%)
1		12 12	> 99 > 99[c]
2		8 12	78 > 99
3		8 12	74 87
4		8 12	71[d] 99[e]
5		12	45[d,f]
6		24	7.5[d,f,g]
7		12	0
8		12	0

[a] Reaction conditions: 0.5 mol% of **1**, 40 °C, solvent: CH_2Cl_2. [b] Determined by ^1H NMR spectroscopy. [c] $CDCl_3$ solvent. [d] Isolated yield. [e] Crystalline residue. [f] White precipitate. [g] Ratio between H-olefin of carboxylic acid and aldehyde.

influence if it is conjugated to an aromatic group (entry 5 and 6).[15] Attempts to recover the catalyst have, so far, been unsuccessful.

We suggest that oxygen from the air may insert into the RC(=O)–H bond. Thus, a peroxyacid may initially be formed, which then rearranges to the carboxylic acid. To the best of our knowledge, other lanthanide catalysts do not catalyse this type of reaction. Thus, $Ln(OTf)_3$[16] and lanthanide alkoxides such as $[La_3(O\textit{t}Bu)_9]$[17] give aldol reaction products, whereas $[Ln\{N(SiMe_3)_2\}_3]$[5] leads to a Tishchenko or an aldol-Tishchenko reaction.

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the DAAD (fellowship for A. Z.) and the CONACyT (postdoctoral fellowship for G. C.-M.) for financial support.

Notes and references

† *Preparation* of **1**: 200 mg (0.66 mmol) of $YCl_3{\cdot}6H_2O$ and 263 mg (1.17 mmol) of Ph_2acacH (dibenzoylmethane) were dissolved in 10 mL of methanol and 147 mg (2.46 mmol) of triethylamine were added to the solution. The mixture was stirred at room temperature for 18 h. A yellow precipitate was formed, which was filtered off and washed with 5 mL of hexane. Yellow crystals were obtained by diffusion after three days [CH_2Cl_2–hexane, (1 : 6)]. Yield: 213 mg (33%). Found: C, 65.40; H, 4.22; $C_{150}H_{115}O_{25}Y_5$ requires: C, 65.22; H, 4.19%. IR (KBr): ν/cm^{-1} 3421 m (νOH), 2059 m, 2677 m, 1599 s (νC=O), 1537 s sh, 1467 s sh, 1430 s, 1297 m sh, 1223 m, 1070 w, 1024 w (νC–O), 720 m sh, 609 w, 525 m. ^1H NMR ($CDCl_3$, 25 °C): δ 2.13 (s, CH), 6.40–7.96 (m, Ph). $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C): δ 31.1 (CH), 127.1 (m-C_6H_5), 128.1 (p-C_6H_5), 128.7 (o-C_6H_5).

‡ *Crystal data* for **1**: $C_{150}H_{115}O_{25}Y_5$, M = 2761.92, tetragonal space group $P4/n$, a = 1944.6(4), c = 1853.0(4) pm, V = 7021(3) × 10^6 pm^3, T = 293(2) K, Z = 2, μ = 2.111 mm^{-1}, 30 524 reflections collected, $R1$ = 0.0643 for 3378 $F > 2(F)$, $wR2$ = 0.1867 for all 3378 data, 300 parameters, all non-hydrogen atoms calculated anisotropic (except C11–C15 and C26–C38); the positions of the H atoms were calculated for idealised positions. The structure was solved and refined using SHELXS-97 and SHELXL-97.[18] CCDC 224900. See http://www.rsc.org/suppdata/cc/b3/b315218a/ for crystallographic data in CIF or other electronic format.

§ To a stirred solution of 0.5 mol% of **1** in 4 mL of CH_2Cl_2 at 25 °C was added 149 μL of cyclohexylcarbaldehyde (1.23 mmol). Then, the solution was stirred at 40 °C for 12 h. The mixture was quenched by addition of 1 N HCl (1 mL), CH_2Cl_2 was removed using a rotary evaporator and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic phase was washed and dried over Na_2SO_4. The solvent was removed under reduced pressure.

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