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S0020-1693(20)31080-X https://doi.org/10.1016/j.ica.2020.119881 DOI: Reference: ICA 119881

To appear in: Inorganica Chimica Acta

Received Date: 30 April 2020 23 June 2020 **Revised Date:** Accepted Date: 30 June 2020



Please cite this article as: H.M. Lapa, M.F.C. da Silva, A.J.L. Pombeiro, E.C.B. Alegria, L.M.D. Martins, Cscorpionate Au(III) complexes as pre-catalysts for industrially significant toluene oxidation and benzaldehyde esterification reactions, Inorganica Chimica Acta (2020), doi: https://doi.org/10.1016/j.ica.2020.119881

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C-scorpionate Au(III) complexes as pre-catalysts for industrially significant toluene oxidation and benzaldehyde esterification reactions

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Graphical Abstract



Highlights

- ► A new C-scorpionate Au(III) was synthesized in water and fully characterized
- ► Au(III) complexes were tested in toluene and benzyl alcohol oxidation reactions
- ► C-scorpionate Au(III) complexes act as active catalysts for peroxidative esterification of benzaldehyde
- ► High selectivity in oxidation and esterification reactions

Abstract

The new Au(III) complex [AuCl₂(Tpms)] (1) and the previously reported [AuCl₂(Tpm)]Cl (2), bearing the potentially tridentate ligands tris(1-pyrazolyl)methanesulfonate $(SO_3C(C_3H_3N_2)_3)$ Tpms) or hydrotris(1-pyrazolyl)methane (HC($C_3H_3N_2$)₃, Tpm), respectively, were synthesized in water at room temperature and characterized using NMR and IR spectroscopy. The molecular structure of 1 was authenticated by single crystal X-ray diffraction analysis. The catalytic performance of the Au(III) complexes was tested, for the first time, in toluene and benzyl alcohol oxidation reactions. The oxidative esterification of benzaldehyde, by-product of toluene oxidation, was further explored. In order to optimize the catalytic systems, the influence of parameters such as temperature, reaction time, amount of pre-catalyst and the presence of additives was evaluated. In the peroxidative (by H₂O₂ or *t*-BuOOH) oxidation reactions, a maximum total yield (benzylic alcohol and benzaldehyde) of 8% for toluene oxidation with pre-catalyst 1 (6 h, 80 °C, H₂O₂ 30% aq. sol.) and a maximum total yield (benzaldehyde and benzoic acid) of 43% for benzyl alcohol oxidation with pre-catalyst 2 (24 h, 80 °C, t-BuOOH 70% aq. sol.) with a selectivity of 72% for benzaldehyde, were obtained. The esterification of benzaldehyde yielded, in the presence of 1, a maximum of 27% and 48% of methyl benzoate, at room temperature and 80 °C, respectively, and with a selectivity of 78% for methyl benzoate.

Keywords: Gold(III) complex; C-scorpionate; toluene oxidation; oxidative esterification; valueadded product.

1. Introduction

The research on gold complexes has recently experienced exponential growth due to their successful use as catalysts for several reactions such as hydrogenation, low-temperature carbon monoxide oxidation, alkane oxidation, C-C coupling, and cyclization, among others [1–5]. However, gold(III) complexes are still underdeveloped when compared to gold(I) complexes. Being a planar coordination center, Au(III) typically has a coordination number of 4, allowing the use of various ligands to form different complexes. The main uses of such complexes are in cancer treatment [4,6] (due to similarities to cisplatin), in C-C coupling reactions and, recently, also in the oxidation [3,7] or hydrocarboxylation of alkanes [8]. After their discovery in 1966 by Trofimenko

[9], B-scorpionates, and later C-scorpionates, have been coordinated to a huge number of transition metals in very different ways [10-12]. C-scorpionates is the general designation for a class of compounds of general formula $[R_{(4-n)}C(R'pz)_n]$ (pz = pyrazol-1-yl; n = 2 or 3) including the tris(pyrazol-1-yl)methane compounds and derivates (n =3). This nomenclature reflects the versatile coordinating behavior of tris(pyrazol-1-yl)methanes when binding to a metal center, resembling **a** scorpion's attack to its pray. C-scorpionates interesting derivatives can be formed either by adding substituents to the pyrazolyl rings or the methine carbon leading to different complexes with characteristic stereochemical and electronic properties. They are isoelectronic with cyclopentadienyl ligands and can present related coordination chemistries. Moreover, they can easily interchange their coordinations [10,11]. C-scorpionate complexes *e.g.*, of V, Fe, Co, Cu, Re or Au can act as catalysts for alkane oxidation reactions, a field that remains underexplored due to the difficulty to activate the C-H bond in such unreactive compounds [10,11].

complexes, to the best of Regarding gold C-scorpionate our knowledge, $[AuMe_2(Tpm)]NO_3.H_2O$ [13], and $[AuCl_2{\kappa^2-RC(R'pz)_3}]Cl$ (R = R' = H, R = CH₂OH, R' = H and $R = H, R' = 3,5-Me_2, pz = pyrazol-1-yl)$ [3], are the only ones reported. The most recent ones, promptly obtained in water at room temperature, were used as efficient catalysts for the peroxidative homo- and heterogeneous oxidation of cyclohexane [3] but were not tested for other catalytic reactions. No other metal complexes using C-scorpionates were tested until now for the oxidation reactions of this work. Thus, there is an opportunity window to test C-scorpionate Au(III) complexes in other important oxidation reactions and to continue the development of this underexplored field of research involving new gold(III) complexes.

Toluene, being a VOC (volatile organic compound) poses an environmental and health hazard. In 2015, 10 kt were emitted to the atmosphere by USA industries [14], while worldwide is estimated that 10 Mt of toluene was emitted [15]. In 2017/18 Australia reported emissions of 1.9 kt of toluene [16]. Oxidation allows to convert toluene in chemical products of added value (Scheme 1) like benzaldehyde used in dyes, perfumes, pharmaceuticals or as an intermediate to form benzoates (*e.g.*, methyl benzoate) [17,18]. The industrial process to obtain benzaldehyde from toluene is performed in very harsh conditions, pressure and with low conversion [17]. Moreover, benzyl alcohol, a by-product of toluene oxidation, is used as solvent of inks, waxes, shellacs and epoxy resins or as a precursor to various esters and ethers to the soap, perfume and flavor industries [19,20]. Oxidation

of benzyl alcohol allows increasing the production of benzaldehyde since this is the main product of the reaction. The oxidative esterification (Scheme 1) allows the formation of esters in a single step from the aldehyde without the formation of the corresponding acid. Methyl benzoate can be obtained by oxidative esterification of benzaldehyde with methanol. It has been used as a solvent for resin and cellulose, air care products, biocides, perfumery, cosmetic and food industry [21–23].



Scheme 1. Valorization reactions for conversion of hazardous toluene.

Thus, herein we report the synthesis and full characterization of a new C-scorpionate gold(III) complex, $[AuCl_2(Tpms)](1)$, and its application, and of its analogue $[AuCl_2(Tpm)]Cl(2)[3]$, as precatalysts for the industrially important selective oxidations of toluene or benzyl alcohol as well as for the esterification of benzaldehyde to methyl benzoate.

2. Experimental

2.1. Materials and methods

Pyrazole (Aldrich), HAuCl₄·3H₂O (Alfa Aesar), methanol (Acros), acetonitrile (Riedel-de-Haën), tetrahydrofuran (Riedel-de-Haën), hydrogen peroxide (30%) (Fluka), *t*-butyl hydroperoxide (70% aq.) (Alfa Aesar), toluene 98% (Aldrich), benzyl alcohol (99.8%) (Sigma-Aldrich), benzaldehyde (98%) (Alfa Aesar), cycloheptanone (99%) (Sigma-Aldrich), nitric acid (65%) (Riedel-de-Haën), nitromethane (Aldrich), diethyl ether (Riedel-de Haën), 2 M *n*-butyllithium (Aldrich), sulfur trioxide trimethylamine complex (Aldrich), sodium carbonate (Panreac),

chloroform (Riedel-de-Haën), celite (Fulka), activated carbon (Panreac), sodium sulfate (Acros), tetrabutylammonium bromide (Acros) were used as received from the supplier, without further purification or drying. Infrared spectra (4000–400 cm⁻¹) were recorded with a Bruker Vertex 70 spectrophotometer in KBr pellets and far infrared spectra (400–200 cm⁻¹) in CsI pellets (wavenumbers are in cm⁻¹). ¹H and ¹³C NMR spectra were recorded with a Bruker Avance III 400 MHz (UltraShieldTM Magnet) spectrometer at ambient temperature. δ values are in ppm. Abbreviations: s, singlet; b, broad; d, doublet; t, triplet; dd, doublet of doublet; C, H, S and N elemental analyses were carried out by the Analytical Services of the Instituto Superior Técnico. Gas Chromatographic (GC) measurements were carried out using an Agilent 7820A series gas chromatograph with FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0,32 nm). Helium was used as carrier gas. UV-Vis measurements were carried out using an Agilent Cary 60 UV-Vis spectrophotometer with double beam and Xenon Flash Lamp (80 Hz) as light source at room temperature using quartz cuvettes with a path length of 1 cm.

2.2. Catalyst precursor preparation

The hydrotris(pyrazol-1-yl)methane (Tpm), lithium tris(pyrazol-1-yl)methanessulfonate (LiTpms) and the complex [AuCl₂(Tpm)]Cl (**2**) were obtained according to the published methods [3,24,25].

Synthesis of the C-scorpionate gold(III) complex [AuCl₂(Tpms)] (1)

LiTpms (0.372 g, 1.3 mmol) was added to distilled water (5 mL) under continuous stirring at room temperature. The gold precursor HAuCl₄•3H₂O (0.500 g, 1.3 mmol) was dissolved in distilled water (5 mL) and added dropwise in a stoichiometric proportion of 1:1 to the ligand solution. A green-yellow solid was obtained, after a few drops added of the gold precursor and was let to stirred for two hours at room temperature. The suspension was filtered by gravity and the solution was concentrated in the rotary evaporator to collect more complex that was still soluble in water. The solid was washed with ethanol and diethyl ether and dried under vacuum. 67% yield was obtained. [AuCl₂(Tpms)] (1) : IR (KBr pellet, cm⁻¹): 3136 [v(CH)], 1610, 1512, and 1286 [v(N=C), v(C=C), v(C–N), HC(pz)₃], 1323 [v(S-C)]. Far-IR (CsI pellet, cm⁻¹): 353 [v_{asym}(Au–Cl)], 326 [v_{sym}(Au-Cl)]. ¹H NMR [$\delta_{\rm H}$ (400.15 MHz, DMSO-d₆, 25 °C)]: 8.13 [d, 3H, ³J_{HH}= 2.9, H(3), HC(pz)₃], 7.40 [s br, 3H, H(5), HC(pz)₃], 6.32 [dd, ³J_{HH}= 3.1, 3H, H(4), HC(pz)₃]. ¹³C NMR [$\delta_{\rm C}$ (400.15 MHz, DMSO-d₆, 25 °C)]: 8.13 [s, C(5), HC(pz)₃], 138.35 [s, C(4), HC(pz)₃], 132.28 [s, C(5), HC(pz)₃], 138.35 [s, C(4), HC(pz)₃], 132.28 [s, C(5), HC(pz)₃], 138.35 [s].

C(3), HC(pz)₃]. Elemental analysis found (calculated): C, 21.35 (21.40); H, <2 (1.62); N, 14.76 (14.98); S, 5.73 (5.71). The C-scorpionate gold(III) complex is soluble in MeCN, DMSO, acetone and MeOH, but, as expected from its synthetic procedure, poorly soluble in water (less than 1×10^{-5} mol/L).

2.3. X-ray crystallographic data

The measurements were performed on a Bruker AXS-KAPPA APEX II PHOTON 100 using Mo Ka radiation of 0.71073 Å) from a fine-focus sealed X-ray source. Full spheres of data were collected using φ and ω scans of 0.5° per frame. Cell parameters were retrieved using Bruker SMART [26] software and refined using Bruker SAINT [26] on all the observed reflections. Absorption corrections were applied using the SADABS [27]. The structures were solved by direct methods using SIR97 package [28] and refined with SHELXL-2018/3 [29]. Calculations were performed using the WinGX System-Version 2018-3 [30]. C-bonded hydrogen atoms were included in the refinement in calculated positions using the riding-model approximation with the Uiso(H) defined as 1.2Ueq of the parent methylene atoms. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms were employed. Crystallographic data are given in Table 1. The structure has been deposited to the Cambridge Crystallographic Data Centre (CCDC 1985561).

	1
Empirical formula	C ₁₀ H ₉ AuCl ₂ N ₆ O ₃ S
Formula weight	561.15
Crystal system	orthorhombic
Space group	P 2 ₁ 2 ₁ 2 ₁
a (Å)	8.2896(4)
b (Å)	10.8130(6)
c (Å)	34.6191(17)
α, β ,γ (°)	90
$V(Å^3)$	3103.1(3)

 Table 1. Crystal data and structure refinement details for 1.

50411141 1	
Z	8
D_{calc} (g/cm ³)	2.402
F000	2112
μ (mm ⁻¹)	9.983
Reflections measured	25963
Obs / Unique reflections	6363 / 4897
Number of parameters	416
R _{int}	0.0769
$R(F) \ (I \ge 2\sigma)$	0.0596
wR (F2) (all data)	0.0931
GOF (F ²)	1.102
Max. and min. residual density	2.031-1.226

2.4. Catalytic studies

2.4.1 Peroxidative oxidation of toluene

In typical conditions, the reactions were carried out in a glass tube at atmospheric pressure and the reaction mixtures for toluene oxidation were prepared as follows: 10 μ mol of pre-catalyst, 5 mmol of toluene, 10 mmol of H₂O₂ (30% aq. sol.) or *t*-BuOOH (70% aq. sol.) were added to 3 mL of MeCN. The mixture was stirred for 24 h at 80 °C. When HNO₃ was used as an additive, the additive/pre-catalyst molar ratios 25-70 were used. For the product analysis, 90 μ L of cycloheptanone (internal standard) and 10 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The resulting mixture was stirred for a maximum of 5 min and then a sample was taken from the organic phase and analyzed by GC using the internal standard method.

The stability of complex 1 was evaluated by comparison of the UV-vis spectra ($6.8 \times 10^{-4} \text{ mol/L}$) of HAuCl₄.3H₂O and of 1 before the reaction and the spectrum of the mixture after the catalytic oxidation reaction.

2.4.2. Peroxidative oxidation of benzyl alcohol

In typical conditions, the reaction mixtures of benzyl alcohol were prepared as follows: 10 μ mol of pre-catalyst, 5 mmol of benzyl alcohol, 10 mmol of *t*-BuOOH (70% aq. sol.) and 50 μ L of nitromethane (internal standard) were added to 3 mL of MeCN. The reaction mixture was stirred for 24 h, at 80 °C and a sample was taken at 5 h and 24 h of reaction time and analyzed by GC using the internal standard method.

2.4.3. Peroxidative esterification of benzaldehyde

In typical conditions, the reaction mixtures of benzaldehyde esterification were prepared as follows: 5 μ mol of pre-catalyst, 5 mmol of benzyl alcohol or benzaldehyde, 10 mmol of *t*-BuOOH (70% aq. sol.) and 50 μ L of nitromethane (internal standard) were added to 1.5 mL of MeCN and 1.5 mL of MeOH. The reaction mixture was stirred for 24 h, at 80 °C and a sample was taken at 5 h and 24 h of reaction time and analyzed by GC using the internal standard method.

3. Results and Discussion

3.1. Syntheses and characterization of the gold(III) complexes

The C-scorpionates hydrotris(1-pyrazolyl)methane $[HC(C_3H_3N_2)_3, Tpm]$ and lithium tris(pyrazol-1-yl)methanesulfonate $[LiSO_3C(C_3H_3N_2)_3, LiTpms]$ were synthesised by following known procedures [24,25] and their characteristic features were confirmed by NMR spectroscopy. Reactions of HAuCl₄•3H₂O with Tpm or the C-functionalized LiTpms derivative were performed in water at room temperature, and led to the new C-scorpionate gold(III) complex, [AuCl₂(Tpms)] (1), and the previously reported complex [AuCl₂(Tpm)]Cl (2) [3] (Fig. 1). As far as we know, complex 1 is the first example of a gold complex bearing the tris(pyrazol-1-yl)methanessulfonate ligand.



Fig. 1 Structures of C-scorpionates Au(III) complexes [AuCl₂(Tpms)] (1) and [AuCl₂(Tpm)]Cl (2).

Compound **1** was analysed by IR and NMR spectroscopy, elemental analysis as well as by single crystal X-ray diffraction. The room temperature ¹H and ¹³C NMR spectra (in DMSO-d₆, Fig. S1-S3) display only three resonances for the pyrazolyl protons and carbons, respectively, that is a single resonance for each type of proton or carbon in each of the position (3, 4 or 5, Fig. 1) of the pyrazolyl ring, suggesting that, in solution, there is an interchange of the uncoordinated pyrazolyl group, which is not distinguishable from the coordinated pyrazolyl ones. The same spectroscopic behaviour was found previously for this type of compounds [3]. The IR spectra of **1** and **2** (Fig. S4-S8) show typical v(C=C) and v(C=N) bands of coordinated pyrazolyl groups at the usual range of 1612-1510 cm⁻¹ [3]. The presence of the chloro ligands is confirmed by the strong and broad v(Au-Cl) at 353 cm⁻¹ and 326 cm⁻¹. Additionally, **1** exhibit a band in the 1372-1335 cm⁻¹ range attributed to v(S=O) of the sulfonate group.

X-ray quality crystals of **1** were obtained by slow evaporation of an acetone solution of the complex. The compound crystallized in the orthorhombic P $2_12_12_1$ space group (Table 1), the asymmetric unit containing two independent complex molecules with similar bond parameters (Fig. 2 and legend). The metal cations exhibit almost perfect square planar geometry constructed from two chloride anions and two N-atoms from two pyrazolyl rings (maximum deviation of 0.051 Å from the N₂Cl₂ least-square plane pertaining to N4 and N6 atoms), therefore leaving coordinatively free a pyrazolyl ring and the sulfonate moiety [31]. The Au–N and Au–Cl bond distances (see Fig. 2 legend) are in the range of those already reported [32–39]. The angle between the least-square planes of the coordinated pyrazolyl rings differ slightly in the two molecules (27.85° for Au1 and 25.79° for Au2), a similar situation occurring for the angle between the least-square plane of the free

pz moiety and the one constructed from the coordinated N- and Cl-atoms (83.16° for Au1 and 84.42° for Au2). The shortest Au…Au distance assumes the value of 5.944(1) Å. In each molecule short intramolecular interactions between the Au(III) and one of the O_{sulfonate} atoms could be found (average Au…O distance of 2.88(1) Å, see Fig. S9) which, being shorter than the sum of the van der Waals radii of gold and oxygen (2.32 and 1.50 Å, respectively) [40] can extend the geometry of the complexes to distorted square-pyramids. The other nearest atom to Au1 is N8, and to Au2 is N2 (Fig. S9) but only in the latter case the obtained distance of 3.41(2) Å may suggest a further extension of the coordination number. The structure of **1** is stabilized by interactions (Fig. S10) involving intramolecular Cl…H and intermolecular O…H contacts.



Fig. 2 Ellipsoid plot of **1**, drawn at 30% probability level. Selected bond distances (Å) and angles (°): Cl1–Au1 2.259(5), Cl2–Au1 2.246(5), Cl3–Au2 2.252(5), Cl4–Au2 2.249(5), Au1–N6 2.045(14), Au1–N4 2.064(13), Au2–N12 2.032(13), Au2–N10 2.032(14); N6–Au1–N4 90.5(5), N6–Au1–Cl2 90.3(4), N4–Au1–Cl2 177.2(4), N6–Au1–Cl1 177.4(4), N4–Au1–Cl1 90.3(4), Cl2–Au1–Cl1 89.0(2), N12–Au2–N10 89.2(5), N12–Au2–Cl4 177.4(4), N10–Au2–Cl4 91.2(4), N12–Au2–Cl3 91.4(4), N10–Au2–Cl3 177.6(4), Cl4–Au2–Cl3 88.3(2).

3.2. Catalytic studies

The C-scorpionate gold(III) complexes [AuCl₂(Tpms)] (1) and [AuCl₂(Tpm)]Cl (2) and, for comparative purposes, the precursor HAuCl₄•3H₂O were screened for *i*) the oxidation of toluene to the corresponding oxidized products, benzaldehyde and benzyl alcohol, *ii*) oxidation of benzyl alcohol to benzaldehyde and benzoic acid and finally *iii*) for the oxidative esterification of benzaldehyde to methyl benzoate (Schemes 2-4). We chose these reactions and experimental conditions due to our longstanding interest in oxidation reactions and previous experience. One class of raw materials is alkyl aromatics; toluene, for example, the simplest member of this class, can be oxidized to benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate as this sequential oxidation is rapid at this temperature [41–43].

Peroxidative oxidation of toluene by 1 and 2



Scheme 2. Oxidation reaction of toluene to benzyl alcohol and benzaldehyde

The peroxidative oxidations of toluene (Scheme 2, Table 2) were undertaken in acetonitrile at 80 °C for 24 h and using *t*-BuOOH (aq. 70%, 2 eq.) or H_2O_2 (aq. 30%, 2 eq.) as oxidants, in the presence of the C-scorpionate gold(III) complex 1 or 2. Under the above-mentioned reaction conditions, toluene is oxidized to yield predominantly benzaldehyde, along with some amount of benzyl alcohol. For longer reaction periods, residual amounts of benzyl benzoate and benzoic acid, among other oxidation products, were detected (by GC-MS). Both complexes show similar catalytic performance, although at different reaction conditions, achieving an overall yield of 6% with selectivity to benzaldehyde of over 85% (Table 2, entries 4 and 13 for complexes 1 and 2, respectively). The previously recognized promoting effect of an acidic medium on the peroxidative oxidation of alkanes catalysed by other C-scorpionates complexes [44, 45] is also observed for the oxidation of toluene in the presence of 1 (entry 1 *vs.* 2) and 2 (entry 12 *vs.* 13). The presence of the acid additive also resulted in an improvement for selectivity to benzaldehyde.

	Catalyst					
Entry	nrecursor	Oxidant	Co-catalyst	Total	Selectivity	vity ^c TON ^d
	precuisor		(n_{acid}/n_{cat})	Yield ^b	Sciectivity	1010
1		H ₂ O ₂ , 30%	-	1.1	73	4
2		H ₂ O ₂ , 30%	HNO ₃ (25)	3.5	83	14
3		H ₂ O ₂ , 30%	HNO ₃ (50)	2.9	70	10
4		H ₂ O ₂ , 30%	HNO ₃ (70)	6.1	87	26
5 ^e	1	H ₂ O ₂ , 30%	HNO ₃ (70)	2.1	43	5
6 ^f	1	H ₂ O ₂ , 30%	HNO ₃ (70)	6.7	83	17
7 ^g		H ₂ O ₂ , 30%	HNO ₃ (70)	3.4	75	25
8^h		H ₂ O ₂ , 30%	HNO ₃ (70)	4.0	78	9
9		<i>t</i> -BuOOH , 70%	-	3.3	51	8
10		t-BuOOH, 70%	HNO ₃ (25)	11.4 ^{<i>i</i>}	36 ^j	20
11 ^k		H ₂ O ₂ , 30%	HNO ₃ (70)	< 0.2	•	-
12		H ₂ O ₂ , 30%		4.5	77	17
12 13		H ₂ O ₂ , 30% H ₂ O ₂ , 30%	- HNO ₃ (25)	4.5 6.3	77 84	17 27
12 13 14		H ₂ O ₂ , 30% H ₂ O ₂ , 30% H ₂ O ₂ , 30%	- HNO ₃ (25) HNO ₃ (50)	4.5 6.3 5.9	77 84 84	17 27 25
12 13 14 15 ^e	2	H ₂ O ₂ , 30% H ₂ O ₂ , 30% H ₂ O ₂ , 30% H ₂ O ₂ , 30%	- HNO ₃ (25) HNO ₃ (50) HNO ₃ (25)	4.5 6.3 5.9 0.3	77 84 84 52	17 27 25 0.6
12 13 14 15 ^e 16 ^f	2	H ₂ O ₂ , 30% H ₂ O ₂ , 30%	- HNO ₃ (25) HNO ₃ (50) HNO ₃ (25) HNO ₃ (25)	4.5 6.3 5.9 0.3 5.9	77 84 84 52 79	17 27 25 0.6 24
12 13 14 15 ^e 16 ^f 17 ^g	2	$\begin{array}{c} H_2O_2, \ 30\% \\ H_2O_2, \ 30\% \end{array}$	- HNO ₃ (25) HNO ₃ (50) HNO ₃ (25) HNO ₃ (25)	4.5 6.3 5.9 0.3 5.9 3.4	77 84 84 52 79 72	17 27 25 0.6 24 24
12 13 14 15 ^e 16 ^f 17 ^g 18 ^h	2	$\begin{array}{c} H_2O_2, \ 30\% \\ H_2O_2, \ 30\% \end{array}$	- HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25)	4.5 6.3 5.9 0.3 5.9 3.4 4.7	77 84 84 52 79 72 78	17 27 25 0.6 24 24 24 9
12 13 14 15 ^e 16 ^f 17 ^g 18 ^h 19	2	H ₂ O ₂ , 30% H ₂ O ₂ , 30% t-BuOOH , 70%	- HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25)	 4.5 6.3 5.9 0.3 5.9 3.4 4.7 2.0 	77 84 84 52 79 72 78 66	17 27 25 0.6 24 24 9 6
12 13 14 15 ^e 16 ^f 17 ^g 18 ^h 19 20	2	H ₂ O ₂ , 30% H ₂ O ₂ , 30% <i>t</i> -BuOOH , 70% H ₂ O ₂ , 30%	- HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) -	4.5 6.3 5.9 0.3 5.9 3.4 4.7 2.0	77 84 84 52 79 72 78 66	17 27 25 0.6 24 24 9 6
$ \begin{array}{r} 12 \\ 13 \\ 14 \\ 15^{e} \\ 16^{f} \\ 17^{g} \\ 18^{h} \\ 19 \\ \hline 20 \\ 21^{1} \\ \end{array} $	2 - HAuCl ₄ .3H ₂ O	$\begin{array}{c} H_2O_2, 30\% \\ t-BuOOH, 70\% \\ \hline H_2O_2, 30\% \\ H_2O_2, 30\% \\ \hline H_2O_2, 30\% \\ \hline H_2O_2, 30\% \\ \hline \end{array}$	- HNO ₃ (25) HNO ₃ (50) HNO ₃ (25) HNO ₃ (25) HNO ₃ (25) -	4.5 6.3 5.9 0.3 5.9 3.4 4.7 2.0	77 84 84 52 79 72 78 66 - 97	17 27 25 0.6 24 24 9 6 - 14

Table 2. Total yield (benzaldehyde and benzyl alcohol) in the oxidation of toluene by *t*-BuOOH (aq. 70%) or H_2O_2 (aq. 30%) and 1 or 2 as catalyst precursors.^{*a*}

^{*a*} Reaction conditions: toluene (5.0 mmol), catalyst precursor **1** or **2** (10 μ mol), *t*-BuOOH (70% aq, 2 eq.) or H₂O₂ (30% aq, 2 eq.) (10 mmol), MeCN (3 mL), 80 °C, 24 h. ^{*b*} Molar yield (%) based on the substrate *i.e.* moles of products (benzaldehyde and benzyl alcohol) determined by GC. ^{*c*}Molar selectivity (%) moles of benzaldehyde per total mmoles. ^{*d*}Turnover number (moles of benzaldehyde per mol of Au pre-catalyst). ^{*e*} Reaction performed at 50 °C. ^{*f*} Reaction performed at 100 °C. ^{*g*}Reaction performed with 5 μ mol of pre-catalyst. ^{*h*}Reaction performed with 20 μ mol of pre-

catalyst. ¹Based on the substrate *i.e.* moles of products (benzaldehyde, benzyl alcohol and benzoic acid) determined by GC. ^jMolar selectivity (%) moles of benzaldehyde per moles of (benzaldehyde + benzyl alcohol + benzoic acid). ^kReaction performed in the presence of Ph₂NH. ^lReaction performed for 6 hours.

The temperature plays an important role in the oxidation of toluene in the presence of **1** and **2**, conceivably due to the high energy normally involved in the activation of little reactive substrates such as hydrocarbons. The total product yield (benzaldehyde + benzyl alcohol) increases as the temperature rises from 50 to 80 °C. For higher temperatures (100 °C) the yield remains almost unchanged, even in some cases decreasing, probably due to the oxidant decomposition (Fig. 3). In the reaction carried out at room temperature, the detected products are residual. Therefore, the temperature of 80 °C was considered the most adequate, combining yield, selectivity, and energy efficiency.



Fig. 3 Effect of temperature on total yield (a) and selectivity (b) of the major products of oxidation of toluene (benzaldehyde + benzyl alcohol) catalyzed by 1 and 2. Reaction conditions: toluene (5.0 mmol), catalyst precursor 1 or 2 (10 μ mol), H₂O₂ (30% aq), MeCN (3 mL), (n_{acid}/n_{cat} = 70 for 1 and n_{acid}/n_{cat} = 25 for 2), 24 h.

The influence of the amount of pre-catalyst (1 and 2) on the oxidation of toluene was investigated. For this study, half (5 μ mol, entries 7 and 17, for 1 and 2, respectively) and twice (20 μ mol, entries 8 and 18, for 1 and 2, respectively) of the amount previously used were tested. According to the results presented in Table 2, it can be concluded that for both catalyst precursors, 1 and 2, the best performance occurs when 10 μ mol is used, both in terms of yield and selectivity.

The oxidant/substrate molar ratio was varied between 1 and 4 and from the results obtained it is observed that the excess of oxidant (2:1) promotes the oxidation reaction as well as selectivity, to a certain extent. The excessive use of oxidant, namely for the ratios 3:1 and 4:1, results in a decrease in yield and selectivity for benzaldehyde possibly due to overoxidation.

In this reaction, comparable results were obtained with the salt HAuCl₄.3H₂O (Table 2, entry 22) what could suggest that similar catalytic active species are formed under the reaction conditions.

The reaction kinetic profile over a 24-hour reaction period was investigated at 80 °C (Fig. 4). In the presence of **1**, the reaction starts slowly, with a total yield of 2.6% but already with a selectivity of 72% indicating that the benzyl alcohol formed during this initial period was readily oxidized to the main product benzaldehyde. After that time, a marked growth in the yield to 8.1% was reached after 6 hours of reaction, where after the total yield starts to decrease, however keeping the selectivity for the aldehyde always above 75% (Figure 4a).

In the case of **2**, a maximum yield of 8.1% is achieved after 10 hours of reaction, then decreasing slightly in the next two hours and remaining constant until completing 24 hours reaction. The selectivity of the reaction has remained relatively constant over time with only slight fluctuations (Figure 4b).

The oxidation reaction carried out in the presence of the salt $HAuCl_{4.}3H_2O$ for 6 hours resulted in a much more modest total yield of 2.6 (Table 2, entry 21) compared to those achieved in the presence of 1 or 2, for the same period.





(a) toluene (5.0 mmol), catalyst precursor **1** (10 μ mol), H₂O₂ (30% aq), MeCN (3 mL), 80 °C, n_{acid}/n_{cat} = 70, 2-24 h. (b) toluene (5.0 mmol), catalyst precursor **2** (10 μ mol), H₂O₂ (30% aq), MeCN (3 mL), 80 °C, n_{acid}/n_{cat} = 25, 2-24 h.

Our catalytic systems have been benchmarked to other Au-based catalytic systems reported previously, and we can essentially highlight their selectivity for one of the toluene oxidation products, benzaldehyde. Kesavan *et al.* reported the activation of the methyl C-H bond in toluene and other derivatives by several Au-Pd alloy nanoparticles [46] using molecular oxygen as the oxidant (10 bar) and carrying out the reactions in the absence of solvent at 160 °C having obtained a maximum conversion of 5.3% and a selectivity of 8.3% for benzaldehyde, for an Au:Pd molar ratio of 1:2. By varying the Au:Pd ratio, it was possible to improve selectivity up to 63%, but in this case the conversion did not go beyond 1.5% [46]. This catalytic system is less selective than ours, always obtaining four oxidation products, benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate, showing that the sequential oxidation is rapid at very high temperatures like the one used in this case.

Peneau *et al.* applied supported gold–platinum nanoalloys Au-Pt/TiO₂ and Au-Pt/C for the oxidation of toluene using *t*-BuOOH (aq. 70%) as the oxidant at 80 °C and achieved conversions of 12.1 and 10.8% and selectivities for benzaldehyde of 1.6 and 1.7%, respectively. Benzoic acid was the major product obtained for both sol-immobilisation materials [47] resulting from the overoxidation of the benzaldehyde formed from benzyl alcohol oxidation. Saima *et al.* applied TiO₂-supported Au and Au-Pd catalysts 1%Au/TiO₂ and 1%Au-Pd/TiO₂ for the oxidation of toluene and achieved conversions of 3.3 and 4.4% and selectivities for benzaldehyde of 47 and 37%, respectively [48]. In all cases mentioned above the Au metal centre is indicated as playing the key role in the catalysis.

The stability of complex **1** in the reaction conditions was evaluated by comparison of its UV-Vis spectra (Fig. S11) before and after the reaction and the one of HAuCl₄.3H₂O. The spectrum of HAuCl₄.3H₂O is completely different from the spectra of complex **1** (before in acetonitrile and after the oxidation reaction), with a characteristic absorption band at 380 nm, suggesting the nondecomposition of **1** into the Au salt.

The mechanism of this reaction should initially involve the formation of oxygen-based radicals HOO[•] and HO[•], as suggested by the oxidation reaction carried out in the presence of the oxygen-radical trap diphenyl amine Ph₂NH resulting in an almost complete reaction inhibition (Table 2, entry 11), upon oxidation or reduction of the oxidant H_2O_2 involving the Au³⁺/Au²⁺ redox couple.

The HO•/HOO• radicals can abstract an H atom from the substrate (CyCH₃) to form the benzyl radical CyCH₂• which then reacts with dioxygen, leading to the CyCH₂OO• peroxyl radical. The peroxyl radical may abstract hydrogen from CyCH₃ and give rise to CyCH₂OOH, whereas CyCHO and CyCH₂OH can be produced by metal-assisted reduction of CyCH₂OO• (for CyCHO) or through CyCH₂OO• dismutation leading to CyCHO and CyCH₂OH (plus O₂).

$Au^{3+} + H_2O_2 \rightarrow HOO^{\bullet} + H^+ + Au^{2+}$	<mark>(1)</mark>
$Au^{2+} + H_2O_2 \rightarrow HO^{\bullet} + Au^{3+} + HO^{-}$	<mark>(2)</mark>
$HO^{\bullet} + CyCH_3 \rightarrow H_2O + CyCH_2^{\bullet}$	<mark>(3)</mark>
$CyCH_2^{\bullet} + O_2 \rightarrow CyCH_2OO^{\bullet}$	<mark>(4)</mark>
$CyCH_2OO^{\bullet} + CyCH_3 \rightarrow CyCH_2OOH + CyCH_2^{\bullet}$	<mark>(5)</mark>
$CyCH_2OO^{\bullet} + Au^2 \rightarrow Au^{3+} + CyCHO + HO^{-}$	<mark>(6)</mark>
$2 \text{ CyCH}_2\text{OO}^\bullet \rightarrow \text{CyCH}_2\text{OH} + \text{CyCHO} + \text{O}_2$	<mark>(7)</mark>

Peroxidative oxidation of benzyl alcohol by 1 and 2



Scheme 3. Oxidation reaction of benzyl alcohol to benzaldehyde and benzoic acid

Benzyl alcohol is one of the products obtained in the oxidation of toluene and as such the study of the catalytic activity of Au(III) scorpionate complexes was extended to the peroxidative oxidation of this substrate.

In this study, several reaction parameters were explored, namely the amount and type of oxidant, reaction time, reaction temperature and pre-catalyst amount, and a total yield (benzaldehyde and benzoic acid) above 45% after 24 hours of reaction, using *t*-BuOOH (aq. 70%, 2 eq.) as the oxidizing agent, could be achieved (Scheme 3). Regarding these tests it was possible to conclude that an excess of oxidant relatively to substrate (2:1) favours the reaction, for *e.g.* the total yield increasing from 14.2 to 43.1% when the stoichiometry is changed from 1:1 to 2:1 (entries 17 and 19, Table 3, respectively), however decreasing the selectivity for benzaldehyde from 92 to 72%. In fact, the selectivity does not diverge much over the first six hours nevertheless the oxidant to substrate molar ratio is 1:1, 2:1 or 4:1. However, for longer periods, selectivity remains constant for the 1:1 molar ratio but decreased for the cases in which an excess of oxidant is used, conceivably due to the oxidation of benzyl alcohol to benzaldehyde and sequential oxidation to benzoic acid.

Entry	Catalyst precursor	n(oxi)/n(subs)	Reaction Time (h)	Total Yield ^b	Selectivity ^c	TON ^d
1		1:1	6	6.2	96	30
2		1:1	24	12.1	93	56
3		2:1	6	11.9	93	56
4		2:1	24	29.3	77	113
5 ^e		2:1	6	6.3	94	29
6 ^e		2:1	24	6.4	87	28
7 f	1	2:1	6	6.7	95	31
81	1	2:1	24	10.6	95	50
9 g		2:1	6	9.1	95	86
10^{g}		2:1	24	33.2	75	248
11^{h}		2:1	6	12.0	94	28

Table 3. Total yield (benzaldehyde and benzoic acid) in the oxidation of benzyl alcohol by t-BuOOH (aq. 70%) and 1 or 2 as catalyst precursors.^{*a*}

			Journal Pre	-proofs		
12^{h}		2:1	24	34.9	71	61
13		3:1	6	6.2	96	36
14		3:1	24	31.2	79	122
15 ⁱ		<mark>2:1</mark>	<mark>6</mark>	<mark>3.1</mark>	<mark>86</mark>	<mark>13</mark>
16		1:1	6	4.9	92	23
17		1:1	24	14.2	92	66
18		2:1	6	11.2	>99	56
19		2:1	24	43.1	72	154
20 ^e		2:1	6	4.1	>99	20
21^e		2:1	24	4.5	>99	22
22 ^f		2:1	6	7.1	96	34
23 ^f	2	2:1	24	9.0	95	43
24 ^g		2:1	6	10.1	95	96
25 ^g		2:1	24	45.6	63	288
26 ^h		2:1	6	8.7	95	21
27^{h}		2:1	24	25.0	84	53
28		3:1	6	11.1	93	52
29		3:1	24	31.3	79	123
30	-	2:1	24	11.8	97	-
31	HAuCl ₄ .3	2:1	24	75.8	32	122
	H ₂ O					

^{*a*} Reaction conditions: benzyl alcohol (5.0 mmol), catalyst precursor **1** or **2** (10 μ mol), *t*-BuOOH (aq. 70%, 2 eq.), MeCN (3 mL), 80 °C. ^{*b*} Molar yield (%) based on the substrate *i.e.* moles of products (benzaldehyde and benzoic acid) determined by GC. ^{*c*}Molar selectivity (%) moles of benzaldehyde per total moles. ^{*d*}Turnover number (moles of benzaldehyde per mol of Au pre-catalyst). ^{*e*} Reaction performed at r.t. ^{*f*} Reaction performed at 50 °C. ^{*g*}Reaction performed with 5 μ mol of pre-catalyst. ^{*h*}Reaction performed with 20 μ mol of pre-catalyst. ^{*i*}Reaction performed in the presence of Ph₂NH.

In this reaction, the effect of temperature was also studied, and it was observed that carrying out the reaction at 80 °C resulted in a greater conversion of benzyl alcohol. At room temperature the conversion did not exceed 6.4 and 4.5% in the presence of **1** and **2**, respectively, even after 24 hours of reaction, however, it should be noted that at this temperature the selectivity is total for

benzaldehyde in the presence of **2**. At 50 °C the conversion went up for both catalytic systems, doubling in some cases the initial value and maintaining the high selectivity for benzaldehyde. Despite the higher yield obtained in the presence of $HAuCl_4.3H_2O$, the selectivity for the desired product (benzaldehyde) is much lower than those achieved with compounds **1** and **2**, suggesting the formation in high amount of the unwanted benzoic acid.



Figure 5. Effect of temperature on total yield of the major products of oxidation of benzyl alcohol (benzaldehyde + benzoic acid) catalyzed by **1** and **2**. Reaction conditions: benzyl alcohol (5.0 mmol), *t*-BuOOH (aq. 70%, 2 eq.), catalyst precursor **1** or **2** (10 μ mol), MeCN (3 mL).

Different amounts of catalyst precursor were tested (5, 10 and 20 μ mol) and it was found that, for complex 1 the use of the different amounts of pre-catalyst does not have much influence on the reaction yield being so possible to decrease the amount used to 5 μ mol. For complex 2, similar conversions were obtained with 5 μ mol of pre-catalyst, significantly improving the TON of the reaction, however with lower selectivity and for that reason most of the tests were performed in the presence of 10 μ mol of pre-catalyst.

Choudhary *et al.* [49] reported the solvent-free oxidation of benzyl alcohol to benzaldehyde by *t*-BuOOH (at 95 °C) over nanogold supported on TiO₂. The TiO₂-supported nanogold catalyst prepared by the homogeneous deposition-precipitation (HDP) showed conversions up to 70% and selectivity for benzaldehyde of *ca.* 60%, after 2 h with an Au loading of 0.02 mmolg⁻¹). Higher gold loading resulted in higher yield but lower selectivity for benzaldehyde. The activity and selectivity (up to 90 and 89%, respectively, after 300 min and at 125 °C) of γ -Al₂O₃ supported Au nanoparticles on the liquid-phase oxidation of benzyl alcohol to benzaldehyde by *t*-BuOOH in the absence of solvent was also reported by Ndolomingo *et al.* [50]

Peroxidative esterification of benzaldehyde by 1 and 2



Scheme 4. Oxidative esterification reaction of benzaldehyde to methyl benzoate and benzoic acid

Benzyl benzoate resulting from the esterification of benzyl alcohol with benzoic acid was detected as a minor by-product in our previous studies related to the oxidation of benzyl alcohol. As proposed by Adnan *et al.* [51] studies carried out in the presence of Au nanoparticles, show that esterification reaction competes with the formation of benzoic acid.

We studied the esterification of benzaldehyde starting from benzyl alcohol (cascade reaction) using 5 mmol of benzyl alcohol, 10 μ mol of pre-catalyst, 1.5 mL of acetonitrile (as solvent), 1.5 mL of methanol and 10 mmol of oxidant (*t*-BuOOH aq. 70%, 2 eq. or H₂O₂ aq. 30%, 2 eq.) for 3, 6 and 24 hours (Scheme 4).

The cascade reaction starts with the oxidation of benzyl alcohol to benzaldehyde followed by the oxidation or esterification reaction of the latter to benzoic acid or methyl benzoate ("in situ"), respectively (Table 4). The reaction was performed at 80 °C and at room temperature being the conversion residual at the latter, requiring heating.

In order to optimize the reaction conditions to produce methyl benzoate, the effect of the presence and the amount of solvent (acetonitrile) was studied, using an equivalent volume of solvent (acetonitrile, 1.5 mL) and esterifying agent (methanol, 1.5 mL) or using exclusively the esterifying agent (methanol, 3 mL). For both cases the use of methanol as solvent and esterification agent appears to be beneficial for the reaction increasing the production of methyl benzoate over 24 hours (entries 6 and 16, Table 4).

Increasing the amount of oxidant leads to an important increase of the total product yield, mainly in the reaction catalyzed by **1** (entry 7 *vs*. entry 1, Table 4), with similar selectivity for the esterification product, suggesting the formation of the oxidation product, the benzoic acid.

Entry		n(oxi)/n(subs)	Reaction Time (h)	Total Yield ^b	Selectivity ^c	TONd
1		2:1	6	0.9	68	3
2		2:1	24	2.1	64	7
3 ^e		2:1	6	0.6	43	1
4 ^e	1	2:1	24	0.9	62	3
5f	1	2:1	6	1.8	74	6
6 ^f		2:1	24	6.5	63	20
7		4:1	6	16.7	61	18
8		4:1	24	1.6	34	28
11		2:1	6	1.9	90	7
12		2:1	24	15.2	34	26
13 ^e		2:1	6	< 0.1	>99	0.3
14 ^e		2:1	24	0.2	>99	1
15 ^f	2	2:1	6	1.6	78	6
16 ^f	L	2:1	24	11.1	61	34
17		4:1	6	3.5	65	11
18		4:1	24	16.7	53	44

Table 4. Total yield in the peroxidative esterification of benzaldehyde (starting from benzylalcohol) using 1 or 2 as catalyst precursors. a

^{*a*} Reaction conditions: benzyl alcohol (5.0 mmol), catalyst precursor **1** or **2** (10 μmol), *t*-BuOOH (aq. 70%, 2 eq.), MeCN (1.5 mL), MeOH (1.5 mL), 80 °C. ^{*b*} Molar yield (%) based on the substrate *i.e.* moles of products (methyl benzoate and benzoic acid) determined by GC. ^{*c*}Molar selectivity (%) moles of methyl benzoate per total moles. ^{*d*}Turnover number (moles of methyl benzoate per mol of Au pre-catalyst). ^{*e*}Reaction performed at r.t. ^{*f*} 3 mL methanol.

This behavior may suggest that the production of benzaldehyde is dominant, thus becoming the limiting step, in the benzyl alcohol oxidation and that the esterification reaction passes through

benzaldehyde and not benzoic acid. Considering that the formation of methyl benzoate is, in this case, a two-step process, and being the formation of benzaldehyde the slow step we decide to explore the esterification reaction directly from benzaldehyde (Table 5) [51].

As in the previous study, the effect of the presence and the amount of solvent (acetonitrile) and esterifying agent (methanol) was explored. Using an equivalent volume of solvent (acetonitrile, 1.5 mL) and esterifying agent (methanol, 1.5 mL) resulted in lower conversion and selectivity for the benzoate (Table 5, entries 1-4 and 13-16, for 1 and 2, respectively), being this reduction more evident in the presence of **1**.

The production of benzoate seems to occur preferentially in the first hours, for e.g. in the case of **1** reaching already a total yield of 48.2% and high selectivity of 78% for this product after the first 3 hours (Table 5, entry 5). For longer periods, the formation of benzoic acid is favored, in the case of pre-catalyst **1** and after 24 hours only the oxidation product was detected (Table 5, entry 4).

Entry	n(oxi)/n(subs)	Reaction	Total Vialdh	Salastivity	TONd
		Time (h)	Total Yleid	Selectivity	IUN"
1 ^e	2:1	6	20.6	52	52
2 ^e	2:1	24	40.9	36	74
3	2:1	6	51.8	68	176
4	2:1	24	f	-	-
5	2:1	3	48.2	78	189
6	0.5:1	3	20.6	78	80
7	1:1	3	24.4	82	100
8	3:1	3	39.9	74	147
9g	2:1	3	32.2	70	226
10^{h}	2:1	3	26.7	73	48
11^{i}	2:1	3	26.8	78	104
12 ^j	<mark>2:1</mark>	<mark>3</mark>	<mark>16.0</mark>	<mark>73</mark>	<mark>21</mark>
13 ^e	2:1	6	24.4	74	80
14 ^e	2:1	24	34.9	46	90

 Table 5. Total yield in the peroxidative esterification of benzaldehyde (starting from benzaldehyde) using 1 or 2 as catalyst precursors.^a

Journal Pre-proofs						
15		2:1	6	32.8	72	117
16		2:1	24	47.4	49	115
17		2:1	3	54.1	53	143
18		0.5:1	3	19.3	72	70
19	2	1:1	3	38.2	79	152
20		3:1	3	17.4	77	67
21 ^g		1:1	3	28.6	77	221
22^{h}		1:1	3	24.5	81	49
23 ^{<i>i</i>}		1:1	3	24.1	82	99
24 ⁱ	-	2:1	3	6.8	10	-
25	-	2:1	3	21.0	69	-
26 ^{<i>i</i>}	HAuCl ₄ .3H ₂ O	2:1	3	26.8	67	90
27	HAuCl ₄ .3H ₂ O	2:1	3	25.1	80	99

^{*a*} Reaction conditions: benzaldehyde (5.0 mmol), catalyst precursor **1** or **2** (10 μmol), *t*-BuOOH (aq. 70%, 2 eq.), MeOH (3 mL), 80 °C. ^{*b*} Molar yield (%) based on the substrate *i.e.* moles of products (methyl benzoate and benzoic acid) determined by GC. ^{*c*}Molar selectivity (%) moles of methyl benzoate per moles of per total moles. ^{*d*}Turnover number (moles of methyl benzoate per mol of Au pre-catalyst). ^{*e*}MeCN (1.5 mL), MeOH (1.5 mL), ^{*f*}the solid product was analysed and mainly benzoic acid was found. ^{*g*}5 μmol of pre-catalyst. ^{*h*}20 μmol of pre-catalyst. ^{*i*}Reaction performed at r.t. ^{*j*}Reaction performed in the presence of Ph₂NH.

The effect of the amount of oxidant was explored and *e.g.* for pre-catalyst **2**, lower oxidant:substrate molar ratio (0.5:1 and 1:1) resulted in lower total yields (19.3 and 38.2%, respectively, entries 18 and 19, Table 5, Fig. 6), though higher selectivities for methyl benzoate of 72 and 79%, suggesting, as expected, a greater extension of the esterification reaction over the oxidation reaction, while an excess of oxidant (2:1) resulted in an increase in total yield (54%, entry 17, Table 5, Fig. 6), accompanied by a decrease in selectivity (53%, entry 17, Table 5, Fig. 6), indicative of a greater formation of benzoic acid. In the case of pre-catalyst **1**, although verified, the effect was not as pronounced (Fig. 6). The results obtained when the reaction is performed with HAuCl₄.3H₂O are lower at 80 °C and similar at room temperature and at 80 °C (Table 5 entries 26 and 27). In both cases the achieved TON is lower than those obtained when the reaction is performed under the same conditions in the presence of complex **1** or **2** (Table 5 entries 5, 11, 19 and 23).



Fig. 6 Yield of the major products of the peroxidative oxidation and esterification of benzaldehyde and selectivity for the esterification product (methyl benzoate) relatively to oxidation product (benzoic acid), catalyzed by **2**. Reaction conditions: benzaldehyde (5.0 mmol), catalyst precursor 2 (10 μ mol), *t*-BuOOH (aq. 70%), MeOH (3 mL), 80 °C, 3 h.

Suzuki *et al* reported [52] the efficient aerobic oxidative esterification of methacrolein in methanol to methyl methacrylate by supported gold-nickel oxides (AuNiO_x) nanoparticles with conversions up to 63% and selectivity to the ester of 97% after 2 hours reaction at 60 °C. Besides that, Hashmi *et al.* reported [53] that mononuclear gold compounds (HAuCl₄) can also be active catalysts in the oxidative esterification of aldehydes, using *tert*-butyl hydroperoxide (*t*-BuOOH) and pyridine as prefered oxidant and performing the reactions during 12 hours at 75 °C afford isolated yields up to 90%.

The mechanism for the peroxidative esterification of aldehydes had been a topic of discussion and two types of mechanisms have been proposed: a coordinative mechanism [54–56] and a radicalar mechanism [57,58]. In our case, a radical mechanism is expected to occur, taking into account the result obtained when added the radical trap Ph_2NH to the reaction medium (Table 5, entry 12), involving the metal-assisted generation of *t*-BuOO• and *t*-BuO• radicals upon oxidation or reduction of the oxidant (*t*-BuOOH), respectively, with the gold cycling between oxidation states +II and +III. The produced oxygen-based radicals are believed to behave as hydrogen atoms abstractors from the aldehydes [53].

4. Conclusions

A neutral C-scorpionate gold(III) complex was synthesised for the first time (previously only cationic C-scorpionate Au(III) compounds were reported). This compound was easily synthesised from the commercially available metallic compound in water and its structure confirmed by single crystal X-ray diffraction, contributing to expand the still underexplored coordination chemistry of gold(III).

A comparison between the catalytic activities of both neutral and cationic compounds was performed using oxidation reactions that have never been carried out in the presence of Au(III) compounds as pre-catalysts.

The possibility of applying such type of complexes as homogeneous catalyst precursors for oxidation, under mild conditions, of toluene and benzyl alcohol and for the esterification of benzaldehyde has also been opened. Moreover, the use of mild conditions for reactions that typically use harsh ones is encouraging for pursuing the search for gold complexes and their application in further reactions following the green chemistry principles.

Appendix A. Supplementary data: Fig. S1. ¹H NRM spectrum for complex 1; Fig. S2. ¹³C NRM spectrum for complex 1; Fig. S3. ¹H NRM spectra for complex 2; Fig. S4. IR spectrum for complex 1; Fig. S5. FAR-IR spectrum for complex 1; Fig. S6. IR spectrum for complex 2; Fig. S7. IR spectrum for complex 2; Fig. S8. FAR-IR spectrum for complex 2.; Fig. S9. Shortest intra- and intermolecular interactions involving the Au metal cations (values in Å) in 1.; Fig. S10. Non-covalent interactions in the molecules of 1 [d(D···A) in Å, \angle D–H···A in °]: C6–H6···Cl1 3.22(2), 110°; C6–H6···O5 3.01(2), 134°; C8–H8···O4 3.39(2), 153°; C9–H9···Cl2 3.20(2), 106°; C11–H11···O5 3.02(2), 112° C16–H16···Cl4 3.21(2), 110°; C19–H19···Cl3 3.22(2), 107°; C19–H19···O1 3.14(2), 137°. Fig. S11. UV-vis spectra of complex 1, before in acetonitrile and after reaction, and of HAuCl₄.3H₂O (6.8x10⁻⁴ mol/L).

Acknowledgments

This research was funded by Fundação para a Ciência e Tecnologia (FCT), project UIDB/00100/2020 of Centro de Química Estrutural, and grants numbers Acção Integrada Luso-Alemã A13/16-DAAD/CRUP, UID/NAN/50024/2019, PTDC/QUI-QIN/29778/2017 and UID/MULTI/04046/2019, and from Instituto Politécnico de Lisboa IPL/2019/STREAM_ISEL Project.

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Highlights

- A new C-scorpionate Au(III) was synthesized in water and fully characterized
- ► Au(III) complexes were tested in toluene and benzyl alcohol oxidation reactions
- ► C-scorpionate Au(III) complexes act as active catalyst for peroxidative esterification of benzaldehyde
- ► High selectivity in oxidation and esterification reactions

Author Contributions: Conceptualization, L.M.D.R.S.M. and E.C.B.A.A.; methodology, L.M.D.R.S.M. and E.C.B.A.A.; investigation, H.M.L. and M.F.C.G.S.; writing-original draft preparation, H.M.L.; writing-review and editing, L.M.D.R.S.M., E.C.B.A.A., M.F.C.G.S. and A.J.L.P.; supervision, L.M.D.R.S.M. and E.C.B.A.A.; project administration, L.M.D.R.S.M. and E.C.B.A.A.; funding acquisition, L.M.D.R.S.M. and E.C.B.A.A.. All authors have read and agreed to the published version of the manuscript.

