Synthesis of Au(III) catalyst and application on oxidation reactions

Hugo M. Lapa [1]

[1]*Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

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In this work, gold(III) complexes bearing C-scorpionate ligands hydrotris(1-pyrazolyl)methane (Tpm) and tris(1-pyrazolyl)methanesulfonate (Tpms) ligands synthesized and characterized and their immobilization on functionalized mesoporous silica supports (SBA-15) was explored. The catalytic performance of the prepared Au complexes ([AuCl$_2$Tpm]Cl (AuTpm) and [AuCl$_2$Tpms] (AuTpms)) was tested in oxidation reactions, namely of toluene, benzyl alcohol, glycerol and sulphur compounds present in diesel. The oxidative esterification of benzaldehyde, by-product of toluene oxidation, was further explored. In order to optimize the various catalytic systems, the influence of different parameters such as temperature, reaction time, amount of catalyst and the presence of additives was evaluated. In the peroxidative (H$_2$O$_2$ or *t*-BuOOH) oxidation reactions of toluene and benzylic alcohol, maximum yields of 8% for toluene with the AuTpms catalyst (6h, 80ºC, aq. 30% H$_2$O$_2$) and a maximum total yield of 43% for benzyl alcohol with the AuTpm catalyst (24 h, 80 °C, t-BuOOH aq. 70%) with a selectivity of 72% for benzaldehyde, were obtained. The esterification of benzaldehyde, maximum yields of 27% and 48% at room temperature and 80ºC, respectively, in the presence of AuTpms and with a selectivity of 78% for methyl benzoate were achieved. The AuTpm and AuTpms catalysts were inactive in the oxidation of sulphur compounds. Preliminary results on glycerol oxidation were also obtained in this work. Immobilization of the complexes on aptes@SBA-15 revealed the leaching of the C-scorpionate complexes and showed no improvement in reaction. In the end it was possible to increase the market value chain of toluene under mild conditions.

Introduction

The research of organometallic gold complexes has experienced an exponential grow over the past years due to their successful use on several reactions such as hydrogenations, low temperature carbon monoxide oxidation, alkane oxidations, C-C couplings, and, cyclization, among others.[1-4] Gold(III) complexes are still undeveloped when compared to gold(I) complexes. Being a planar complex, it typically has a coordination number of 4, allowing the use of various ligands to form different complexes. The main uses of these complexes are in C-C coupling reactions and as cancer treatments [5] due to similarities to cisplatin and recently used successful in oxidation of cyclohexane. [1]

Scorpionate ligands have been an interesting topic of research over the past decades. Since their discover in 1966 by Trofimenko, the B-scorpionates and later the C-scorpionates have been coordinated to various transition metals in very different ways. [6] [7] Scorpionates are interesting because of all the derivates that can be formed either by adding substituents to the pyrazolyl rings or changing the R at the methine carbon allowing different complexes with different stereochemical and electronic proprieties to be form. These C-scorpionates complexes have been used in several reactions in particularly in oxidation. In fact, tris(pyrazol-1-yl)methane complexes of for example V, Fe, Cu and Re can act as catalysts for alkane oxidation reactions, a field that still is very unexplored due to the in activating the C-H bond in such unreactive compounds. [8] [9]

As a matter of fact, oxidation is one of many reactions that can add value to certain chemical products like toluene or glycerol and even achieve a low-sulphur diesel in mild conditions.

Toluene being a VOC poses an environmental and health hazard. In 2011, 826 thousand tons were emitted to the atmosphere in the USA alone. [10] Oxidation allows to convert toluene in chemical products of greater value like benzaldehyde used in the dyes, perfumes, pharmaceuticals or as intermediate to form benzoates like methyl benzoate. [11] [12]

Glycerol is formed as a sub product of the biodiesel industry. This glycerol comes highly contaminated with salts, methanol, and ashes. The purification process is very expensive. Moreover, it is only used on a certain amount of the glycerol that is totally produced. The rest is used as a fuel for industry or simply thrown away due to its low value. So, oxidation is a way to produce valuable chemical products from raw materials that has very little or no market value. From all the products that can be obtain from the oxidation of glycerol, dihydroxy acetone (DHA), lactic acid, tartronic acid, glycoxylic acid, oxalic acid and glycolic acid are some of the most valuable and requested by the cosmetic, perfumery and pharmaceutical industries. [13-15]

The search for low sulphur content diesel is increasing due to the environmental impact of sulphur oxides present in the engine exhaust emissions. Hydrodesulfurization is the main process used in the petroleum industry but due to the high energy and hydrogen consumption and the difficulty in hydrogenating aromatic sulphur compounds, the search of alternative methods continues. Oxidative desulfurization (ODS) combined with extraction is considered the most promising process to reduce the sulphur content in diesel. The reaction can be carried out at mild conditions, with green oxidants like H_2O_2 and t-BuOOH (TBHP), at temperatures lower than 100 °C and atmospheric pressure. [16-20]

Therefore, the synthesis of a new C-scorpinate gold(III) complex its potential as a catalyst in several oxidation reactions were studied.

Experimental

General materials and procedures

Pyrazole (Aldrich), $HAuCl_4 \cdot 3H_2O$ (Alfa Aesar) acetonitrile (Riedel-de-Haën), tetrahydrofuran (Riedel-de-Haën), hydrogen peroxide (30%) (Fluka), nitric acid (65%) (Riedel-de-Haën), nitromethane (Aldrich), diethyl ether (Riedel-de Haën), benzothiophene (BT), dibenzothiophene (DBT) (Aldrich), 4,6 dimethyldibenzothiophene (4,6-DMDBT, Aldrich), (3-aminopropyl) triethoxysilane (aptes, Aldrich), anhydrous toluene 99.8% (Aldrich), hydrochloric acid (HCl, Fisher Chemicals), pluronic P123 (Aldrich) tetraethoxysilane (TEOS, Aldrich), n-octane (Aldrich), n-Butyllithium 2M (Aldrich), sulfur trioxide trimethylamine complex (Aldrich), sodium carbonate (Panreac), chloroform, celite (Fulka), active carbon (Panreac), sodium sulfate (Acros), tetrabutylammonium bromide (Acros) .

The hydrotris(pyrazol-1-yl)methane (Tpm), tris(pyrazol-1-yl)methanessulfonate (Tpms), SBA-15, aptes@SBA-15 and [AuCl2Tpm]Cl (AuTpm) were obtained according to the published methods. [1] [21-24]

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).

^{1}H and ^{13}C 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; d, doublet; t, triplet; dd, doublet of doublet;

The inductively coupled plasma (ICP) and 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 a Agilent 7820A series gas chromatograph with FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0,32 nm) and a GC-FID Bruker 430-GC-FID with a capillary column (SPB-5 Supelco, column length: 30 m; internal

diameter: 0,25 nm). Helium and Hydrogen were used as carrier gas, respectfully.

Crystallography data was obtained by Dr. Maria Fátima Guedes da Silva using a Bruker D8 Quest Single Crystal Diffractometer.

The microwave reactions were performed at Anton Paar Monowave 300 with rotational system and IR temperature detector.

Synthesis of C-scorpionate gold(III) complex [AuCl2Tpms]

The Tpms was added to distilled water under continuous stirring at room temperature. The gold precursor $HAuCl_4 \cdot 3H_2O$ was dissolved in distilled water and added dropwise in a stoichiometric proportion of 1:1 to the ligand solution. A green-yellow solid was obtained. The suspension was filtered by gravity and the solution was concentrated in the rotary evaporator to collect more complex that is still soluble in water. The solid was washed with ethanol and ether and dried under vacuum. 67% yield was obtained.

Catalytic activity tests

The oxidation reactions were carried out in a glass tube under atmospheric pressure. Under typical conditions, the reaction mixtures of toluene were prepared as follows: 10 μmol of catalyst were added to 3 mL of NCMe, 5 mmol of toluene, 10 mmol of H_2O_2 at 30% and 50% or t-BuOOH 70%. The mixture was stirred for 24 h, at 80 °C. When HNO_3 was used as an additive the additive/catalyst ratio was used between 25-715. For the product analysis, 90 μL 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 analysed by GC using the internal standard method.

Under typical conditions, the reaction mixtures of benzyl alcohol were prepared as follows: 10 μmol of catalyst were added to 3 mL of NCMe, 5 mmol of benzyl alcohol, 1180 μL of t-BuOOH 70% and 50 μL of nitromethane (internal standard). 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 analysed by GC using the internal standard method.

Under typical conditions, the reaction mixtures of benzaldehyde esterification were prepared as follows: 5 μmol of catalyst were added to 1,5 mL of NCMe, 1,5 mL of MeOH, 5 mmol of benzyl alcohol or benzaldehyde, 1180 μL of t-BuOOH 70% and 50 μL of nitromethane (internal standard). 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 analysed by GC using the internal standard method.

Under typical conditions, the reaction mixtures of oxidative desulfurization were prepared as follows: 1 mL of NCMe, 1 mL of diesel model containing BT, DBT, 4-MDBT and 4,6-DMDBT 500 ppm each making a total of 2000 in n-octane and. 3 μmol of catalyst. The reaction mixture is let to stirred for 10 min to achieve the liquid-liquid equilibrium and then 75 μL of H_2O_2 30% or 100 μL of t- 70% is added. 20 μmol of samples were taken at 10, 30, 60, 120, 180, 240 min and added to a 20 μmol tetradecane solution (internal standard) and analysed by GC by the internal standard method.

Results

Characterization of scorpionate ligands.

The ligands were analysed by NMR spectroscopy and the characterization previously reported at [21] [22] was confirmed.

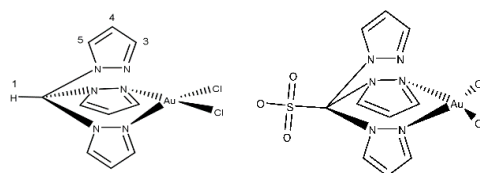**Characterization of C-scorpionate gold(III) complexes**

Figure 1 – Left- Complex 1 [AuCl2Tpm]Cl; Right - Complex 2 [AuCl2Tpms]

AuTpm was analysed by NMR spectroscopy and the characterization previously reported at [1] was confirmed. AuTpms was analysed by single crystal x-ray, IR spectroscopy, NMR spectroscopy and elemental analysis.

[AuCl$_2$Tpms] (2) : 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)]. ^{1}H NMR [δ$_H$ (400.15 MHz, DMSO-d$_6$, 25 °C)]: 8.12 [d, 3H, H(3), HC(pz)$_3$], 7.39 [d, 3H, H(5), HC(pz)$_3$], 6.32 [dd, 3H, H(4), HC(pz)$_3$]. ^{13}C NMR [δ$_C$ (400.15 MHz, DMSO, 25 °C)]: 96.34 [1C, HC(pz)$_3$], 105.87 [3C, C(4), HC(pz)$_3$], 132.28 [3C, C(5), HC(pz)$_3$], 138.35 [3C, 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 IR spectra of AuTpm and AuTpms show typical v(C=C) and v(C=N) bands of coordinated pyrazolyl groups at the usual range of 1612-1510 cm^{-1}. [1] The presence of chloride ligands is confirmed by the strong intensity and broad v(Au-Cl) band at *ca.* 360 cm^{-1}. Moreover, AuTpms exhibits a band in the 1372-1335 cm^{-1} range attributed to v(S=O) from the sulfonate present on the ligand.

The room temperature ^{1}H or ^{13}C NMR spectra (in CD$_3$OD or DMSO-d$_6$) displays only 3 resonances for the pyrazolyl protons or carbons (a single resonance for each type of proton or carbon representing each position of the ring 3, 4 or 5), suggesting that, in solution, there is an interchanging of the uncoordinated pyrazolyl group, which is not indistinguishable from the coordinate pyrazolyl. [1]
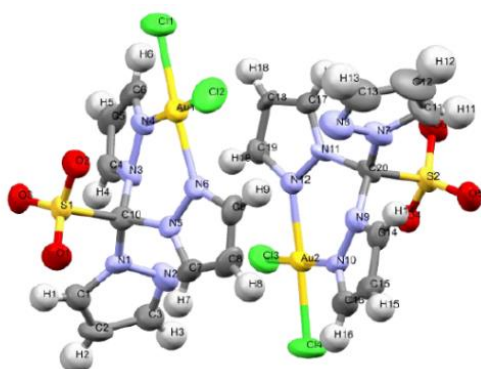
X-ray structure of [AuCl$_2$Tpms]

Figure 2 -ORTEP diagram of [AuCl$_2$Tpms]

Table 1 - Selected bond distances (Å) and angles (°) for AuTpms

Bond Distances	
Au(1)-Cl(1)	2.26
Au(1)-Cl(2)	2.25
Au(1)-N(6)	2.05
Au(1)-N(4)	2.06
C(10)-N(1)	1.44
C(10)-N(3)	1.47
C(10)-N(5)	1.48
C(10)-S(1)	1.86
Bond angles	
Cl(2)-Au(1)-Cl(1)	89.2
N(4)-Au(1)-N(6)	90.5
Cl(1)-Au(1)-N(4)	90.3
Cl(2)-Au(1)-N(6)	90.3
N(3)-C(10)-N(1)	107
N(5)-C(10)-N(3)	111
N(5)-C(10)-N(1)	106
S(1)-C(10)-N(5)	110
S(1)-C(10)-N(3)	111
S(1)-C(10)-N(1)	113

Crystals of [AuCl$_2$Tpms] were grown on an acetone solution of the complex. Figure 2 shows an ORTEP diagram and selected bonds and angles are collected in Table 1. The gold is coordinated by two of the three pyrazolyl rings and two chloride atoms in a square planar arrangement. The data obtained showed that the crystal belongs to the orthorhombic system, having three perpendicular crystallographic axes with different lengths between them. The average Au-N bond distance is 2,06 Å and the average bond distance for Au-Cl is 2,25 Å both being in the range of other similar bonds reported. [25-27]

Catalytic activity
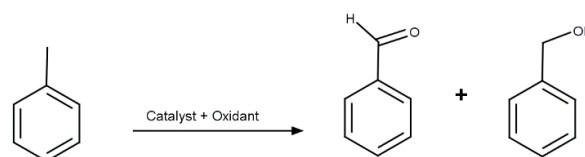
Toluene oxidation

Figure 3 - Oxidation of toluene to benzaldehyde and benzyl alcohol

The C-scorpionate gold(III) complexes **1** and **2** act as catalysts for the peroxidative oxidation of toluene to benzaldehyde and benzyl alcohol. Both complexes show similar activity, although at different conditions, achieving an overall yield of 6% with selectivity to benzaldehyde of over 80% (Table 2, entries 5 and 7 for complexes **1** and **2** respectfully).

The previously recognized promoting effect of an acidic medium on the peroxidative oxidation of alkanes

catalysed by C-scorpionates complexes like iron, and vanadium [28] [29] complexes is indeed observed the contrary to the result obtain for the complex **1** when used on cyclohexane oxidation, (Table 2 entries 1, 5, 6). [1]

The effect of the reaction time on the yield of the reaction was investigated. Is possible to observe that complex **2** is much more active, achieving 8.1% on overall yield with 82% of selectivity to the benzaldehyde in just 6 hours, while complex **1** can achieve similar results within 8 hours. This shows it is possible to achieve a highly selectivity process in a maximum of 8 hours in mild conditions.
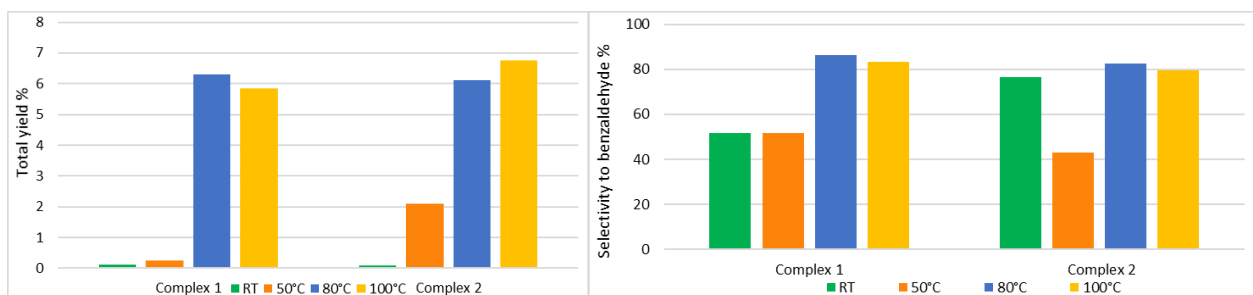
Table 2 - Oxidation of toluene [a]

Entry	Oxidant	n(oxidant)/n(raw material)	nHNO$_3$/n(catalyst) x10^{-3}	Catalyst	Total yield(%) [b]	Selectivity (%) [c]	Ton [d]
1	H$_2$O$_2$ 30%	2	0	1	4.5	77	17
				2	1.1	73	4
2	TBHP 70%	2	0	1	2.0	66	6
				2	3.3	51	8
3	H$_2$O$_2$ 50%	2	0	1	0.5	50	1
				2	0.4	63	1
4 [e]	TBHP 70%	2	25	2	11.4	36	20
5	H$_2$O$_2$ 30%	2	25	1	6.3	84	27
				2	3.5	83	14
6	H$_2$O$_2$ 30%	2	50	1	5.9	84	25
				2	2.9	70	10
7	H$_2$O$_2$ 30%	2	70	1	6.2	87	27
				2	6.1	87	26
8	H$_2$O$_2$ 30%	2	140	1	5.4	69	19
				2	6.4	78	25
9	H$_2$O$_2$ 30%	2	360	1	5.0	88	22
				2	4.9	86	25
10	H$_2$O$_2$ 30%	2	715	1	8.0	94	38
				2	2.5	68	21
11 [f]	H$_2$O$_2$ 30%	2	25	1	0.1	52	0.2
			70	2	<0.1	76	0.3
12 [g]	H$_2$O$_2$ 30%	2	25	1	0.3	52	0.6
			70	2	2.1	43	5
13 [h]	H$_2$O$_2$ 30%	2	25	1	5.9	79	24
			70	2	6.7	83	27
14 [i]	H$_2$O$_2$ 30%	2	25	1	3.4	72	24
			70	2	3.4	75	25
15 [j]	H$_2$O$_2$ 30%	2	25	1	4.7	78	9
			70	2	4.0	78	8
16	H$_2$O$_2$ 30%	1	25	1	5.1	80	20
			70	2	5.2	86	22
17	H$_2$O$_2$ 30%	3	25	1	5.6	77	21
			70	2	4.1	80	16
18	H$_2$O$_2$ 30%	4	25	1	4.8	75	18
			70	2	5.3	79	21
19 [k]	H$_2$O$_2$ 30%	2	25	1	3.5	87	16
			75	2	3.3	89	16

[a]Reaction conditions (unless stated otherwise): acetonitrile (3.0 mL), toluene (5.0 mmol), 80 °C, 24 h, 10 µmol of catalyst. Percentage of yield, selectivity and TON determined by GC analysis (after extraction with diethyl ether, 10 mL, and using cycloheptanone as standard). [b] Molar yield (%) based on the substrate *i.e.* moles of products (benzaldehyde and benzyl alcohol). [c] Molar selectivity (%) moles of benzaldehyde per moles of (benzaldehyde + benzyl alcohol). [d] Turnover number (moles of benzaldehyde per mol of Au catalyst). [e] total yield and selectivity include the formation of benzoic acid. [f] reaction at r.t. [g] reaction at 50°C. [h] reaction at 100°C. [i] reaction with 5 µmol of catalyst. [j] reaction with 20 µmol of catalyst. [k] using the complexes supported on aptes@SBA-15.

Figure 4- Effect of temperature on the total yield and selectivity of the reaction. (Table 2 entries 5, 7, 11-13)

The effect of temperature on the overall yield was investigated and is shown in Figure 4. For temperatures below 80 ⁰C, the reaction is inefficient, revealing that the energy required to oxidize toluene is high (Table 2 entries 11, 12). For temperatures higher than 80 °C, there is no improvement, perhaps due to the faster decomposition of hydrogen peroxide, resulting in a underperforming oxidation (Table 2 entry 13).

Comparing the results obtained for the homogeneous and heterogeneous catalysts showed that the homogeneous lead to better yield on the overall reaction (Table 2 entries 5, 7 ,19) and the alteration of the heterogeneous catalysts when acid was added was observed.
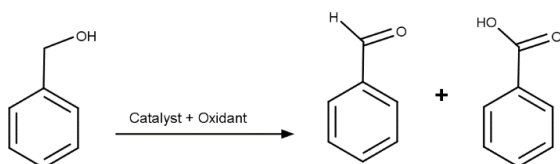
Benzyl alcohol oxidation

Figure 5 - Oxidation of benzyl alcohol to benzaldehyde and benzoic acid

The C-scorpionate gold(III) complexes **1** and **2** act as catalysts for the peroxidative oxidation of bezyl alcohol to benzaldehyde and benzoic acid. Complex **1** is the most active catalyst, achieving a total yield of 43% with 72 % selectivity to the benzaldehyde and a TON of 154 after 24 hours (Table 3, entry 4).

Table 3 - Oxidation of benzyl alcohol [a]

Entry	Oxidant	n(oxi)/n(r)	Catalyst	T.Y. (%)[b]	S.(%)[c]	Ton[d]
1[e]	H₂O₂ 30%	1.7	1	16.9	81	68
			2	10.7	86	46
2[f]	H₂O₂ 30%	1.7	1	22.1	64	71
			2	26.7	66	86
3[e]	TBHP 70%	1.7	1	11.2	100	56
			2	11.9	93	56
4[f]	TBHP 70%	1.7	1	43.0	72	154
			2	29.3	77	113
5[e]	TBHP 70%	0.9	1	4.9	92	23
			2	6.2	96	30
6[f]	TBHP 70%	0.9	1	14.2	92	66
			2	12.1	93	56
7[e]	TBHP 70%	2.6	1	11.1	93	52
			2	6.2	96	30
8[f]	TBHP 70%	2.6	1	31.3	79	123
			2	31.2	79	122
9[e)g]	TBHP 70%	1.7	1	4.1	100	20
			2	6.3	94	29
10[f)g]	TBHP 70%	1.7	1	4.5	100	22
			2	6.4	87	28
11[e)h]	TBHP 70%	1.7	1	7.1	96	34
			2	6.7	95	31
12[f)h]	TBHP 70%	1.7	1	**9.0**	**95**	**43**
			2	10.6	95	50
13[e)i]	TBHP 70%	1.7	1	10.1	95	96
			2	9.1	95	86
14[f)i]	TBHP 70%	1.7	1	45.6	63	288
			2	33.2	75	248
15[e)j]	TBHP 70%	1.7	1	8.7	95	21
			2	12.0	94	28
16[f)j]	TBHP 70%	1.7	1	25.0	84	53
			2	34.9	71	61
17[f]	TBHP 70%	1.7	-	11.8	98	-

[a]Reaction conditions (unless stated otherwise): acetonitrile (3.0 mL), benzyl alcohol (5.0 mmol), 80 °C, 24 h, 10 μmol of catalyst. Percentage of yield, selectivity and TON determined by GC analysis using nitromethane as standard. [b] Molar yield (%) based on the substrate *i.e.* moles of products (benzaldehyde and benzoic acid). [c] Molar selectivity (%) moles of benzaldehyde per moles of (benzaldehyde + benzoic acid). [d] Turnover number (moles of benzaldehyde per mol of Au catalyst). [e] 5 hours sample [f] 24 hours sample [g] reaction at r.t. [h] reaction at 50°C. [i] reaction with 5 μmol of catalyst. [j] reaction with 20 μmol of catalyst.

It was observed that for complex **1** after 5 hours the H_2O_2 is a better oxidant than *t*-BuOOH (Table 3, entries 1, 3) but when compared to the result obtained after 24 hours, the best result occurs with the use of t-BuOOH with much

higher TON than when used H_2O_2 30% was used (Table 3, entries 2, 4).

The effect of the quantity of oxidant was investigated. Increasing the quantity of oxidant slightly improved the total yield for complex **1**, but the improvement obtained was not substantially enough to justify the use of that amount of oxidant (Table 3, entry 8).

The effect of temperature was studied. As before, when temperatures below 80 ºC were used, the yield decreases significantly; the yield at 50 ºC after 24 hours was the same as at 80 ºC after 5 hours (Table 3, entries 3, 12). At room temperature, the reaction did not improve or react more than 5 hours seeing that the yield is constant during the time, while at 50 °C and 80 °C there is a yield increase between 5 and 24 hours of reaction. (Table 3, entries 3, 4, 9 - 12). Although the oxidation of an alcohol occurs better at lower temperatures, when compared to alkanes, it is only possible to achieve a greater overall yield near 80 °C

Finally, comparing the reaction with and without catalyst it is possible to determine that the production of benzaldehyde is much higher when any of the complexes is used.
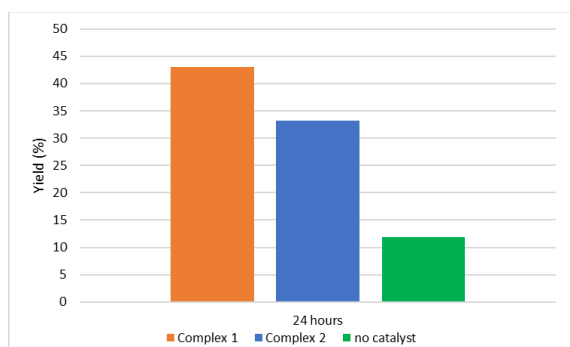

Figure 6 – Comparison of total yield for the best conditions obtain for the catalyst and the reaction yield without catalyst. (Table 3 entries 4, 14, 17)
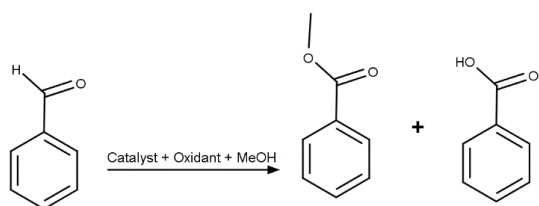
Oxidative esterification of benzaldehyde

Figure 7 - Oxidative esterification of benzaldehyde to methyl benzoate

The C-scorpionate gold(III) complexes **1** and **2** act as catalysts for the peroxidative oxidative esterification of benzaldehyde to methyl benzoate and benzoic acid. First, the esterification using benzyl alcohol as reactant it was investigated. Being a two-step reaction, oxidation of benzyl alcohol to benzaldehyde then esterification to methyl benzoate, it is observed that at room temperature, the reaction occurs with a low yield due to the need to obtain benzaldehyde first from benzyl alcohol (Table 4, entries 1 – 4). Doubling the amount of oxidant increases the yield, but not enough to justify such an amount. (Table 4, entries 7 – 10)

Table 4 - Oxidative esterification of benzaldehyde with methanol [a)] [b)]

Entry	Oxidant	n(oxi)/n(rm)	Catalyst	T.Y. (%)[b)]	S.(%)[c)]	Ton[d)]
1[f)]	TBHP 70%	1.7	1	1.9	90	7
			2	0.9	68	3
2[g)]	TBHP 70%%	1.7	1	15.2	34	26
			2	2.2	64	7
3[f)h)]	TBHP 70%	1.7	1	<0.1	100	0.3
			2	0.6	43	1
4[g)h)]	TBHP 70%	1.7	1	0.2	100	1
			2	0.9	62	3
5[f)]	H_2O_2 30%	1.7	1	2.7	38	5
			2	1	40	2
6[g)]	H_2O_2 30%	1.7	1	12.4	30	19
			2	4.4	30	6
7[f)i)]	TBHP 70%	1.7	1	1.6	78	6
			2	1.8	74	6
8[g)i)]	TBHP 70%	1.7	1	11.1	61	34
			2	6.5	63	20
9[f)i)]	TBHP 70%	3.4	1	3.5	65	11
			2	5.9	61	18
10[g)i)]	TBHP 70%	3.4	1	16.7	53	44
			2	16.7	34	28
11[f)]	TBHP 70%	1.7	1	33	72	117
			2	52	68	176
12[g)]	TBHP 70%	1.7	1	47	49	115
			2 r)	-	-	-
13[f)j)]	TBHP 70%	1.7	1	24	74	90
			2	21	50	52
14[g)j)]	TBHP 70%	1.7	1	35	46	80
			2	41	36	74
15[k)]	TBHP 70%	1.7	1	19.2	79	76
			2	21.7	65	71
16[m)]	TBHP 70%	1.7	1	26.0	65	85
			2	35.3	80	142
17	TBHP 70%	1.7	1	54.0	53	143
			2	48.2	78	189
18[n)]	TBHP 70%	1.7	1	40.5	67	137
			2	46.7	76	185

7

Entry	Oxidant	Ratio		Yield	Selectivity	TON
19[o)]	TBHP 70%	1.7	1	61	45	137
			2	35.9	55	99
20	TBHP 70%	0.5	1	19.3	72	70
			2	20.6	78	80
21	TBHP 70%	0.9	1	38.2	79	152
			2	24.4	82	100
22	TBHP 70%	2.6	1	17.4	77	67
			2	39.9	74	147
23[p)]	TBHP 70%	0.9	1	28.6	77	221
		1.7	2	32.2	70	226
24[q)]	TBHP 70%	0.9	1	24.5	81	49
		1.7	2	26.7	73	48
25[h)]	TBHP 70%	0.9	1	24.1	82	99
		1.7	2	26.8	78	104
26	TBHP 70%	1.7	-	20.8	31.3	-
27[h)]	TBHP 70%	1.7	-	6.8	90	-

[a]Reaction conditions (for entries 1-10): acetonitrile (1.5 mL), methanol (1.5 mL), benzyl alcohol (5.0 mmol), 80 °C, 24 h, 10 µmol of catalyst. Percentage of yield, selectivity and TON determined by GC analysis using nitromethane as standard. [b)] Reaction conditions (for entries 11-27): acetonitrile (2 mL), methanol (3 mL), benzaldehyde (5.0 mmol), 80 °C, 3 h, 10 µmol of catalyst. Percentage of yield, selectivity and TON determined by GC analysis using nitromethane as standard. [c)] Molar yield (%) based on the substrate *i.e.* moles of products (methyl benzoate and benzoic acid). [d)] Molar selectivity (%) moles of methyl benzoate per moles of (methyl benzoate + benzoic acid). [e)] Turnover number (moles of methyl benzoate per mol of Au catalyst). [f)] 5 hours sample [g)] 24 hours sample [h)] reaction at r.t. [i)] 0 mL acetonitrile and 3 mL methanol. [j)] 1.5 mL acetonitrile and 1.5 mL methanol. [k)] 1 hour's sample [m)] 2 hours sample [n)] 4 hours sample [o)] 8 hours sample [p)] reaction with 5 µmol of catalyst. [q)] reaction with 20 µmol of catalyst. r) a solid was form at the end of the reaction, when dissolved and analysed by GC only benzoic acid was found.

The only parameter that influenced the yield or the selectivity was the quantity of methanol in the reaction. When all the solvent was substituted with methanol the complex **2** increased the yield obtained and complex **1** the selectivity to methyl benzoate. (Table 4 entries 1, 2, 7, 8) As reported, since the oxidation of benzyl alcohol is the slow step of the reaction, the esterification was promptly investigated using benzaldehyde as reactant. First, influence of the quantity of methanol in the reaction was investigated, since previously, it was an important factor. Substituting the solvent with methanol improves not only the yield, but also the selectivity of the

reaction. When comparing the results for 5 and 24 hours, it's possible to see by the TON that the reaction did not produce any more methyl benzoate with complexes **1** and **2** and only acid benzoic was produced. Analysing the kinetics of the reaction, it's possible to determine that the reaction, is complete after only 3 hours, the rest of the time being used for the oxidation of benzaldehyde to benzoic acid.
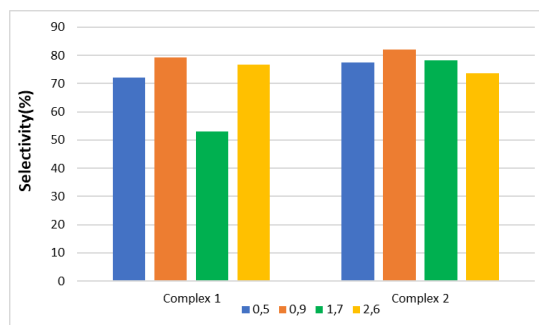

Figure 8 - Effect of the quantity of oxidant on the selectivity to methyl benzoate. (Table 4 entries 17, 20-22)

The effect of the quantity of oxidant was studied. By changing the quantity to a ratio of 0.9, it was possible to improve the production of methyl benzaldehyde by increasing the selectivity of the reaction. Even though some yield was lost, this was compensated by not producing benzoic acid and more methyl benzoate. For complex **2**, the 1.7 ratio is considering the best, having the higher TON. (Table 4 entries 17, 20-22, Figure 8)

The effect of temperature was also investigated. The reaction at room temperature is very successful, achieving around 25% of yield with more than 78% of selectivity. The reaction at 80°C has a higher yield of methyl benzoate. To determine the best temperature a further economic analysis is needed, to assess and compare the cost of production versus the gain in product for each temperature. At least when compared the reaction without the presence of catalyst at both temperatures is evident that the catalysts improve the production of methyl benzoate, achieving higher yields and even with higher selectivity.
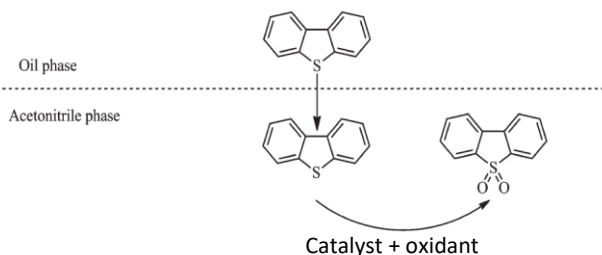
Oxidative desulfurization

Figure 9 - Extraction and oxidation of sulphur compounds presents on diesel. Adapted from [30]

Both complexes where tested in the system and conditions previously optimize by the Balula *et. al.* group [19] [18] [31] being both inactive to the reaction. The effect of the quantity of catalyst and the type of oxidant (H_2O_2 and *t*-BuOOH) used were tested. The inactivity of the catalysts may be caused by the lack of energy needed to activate the catalysts for the oxidation. Since the increase of temperature can cause oxidation of diesel compounds, which is not favourable. Another explanation can be mechanism of the reaction. Since this is usually a coordinative mechanism [30] [32] [33] and since both complexes are gold(III) complexes usually having 4 ligands, it is speculated that the coordination sphere is full not allowing it to catalyse via a coordinative mechanism. There are reports of a radicalar mechanism with acetic acid as co-catalyst, which was not tested in this study, or where the excess oxidant inhibiting the oxidation of sulphur compounds. [34-36]

Glycerol oxidation

During this work, the oxidation of glycerol was investigated, and some preliminary results were found. Not having all the products that are possible to obtain during the reaction to analyse by GC or the possibility of using GC-MS only some of them were accounted for. Since glycerol is an alcohol, its oxidation occurs very easily, and the products formed are even more reactive than the raw material. Using the mechanism scheme proposed by Katryniok *et.al.* [15] and the results that were obtained it's possible to conclude that the reaction is occurring at a fast pace, having one of the last products obtainable by oxidation, oxalic acid, after half an hour.

. It's also possible to conclude that the complexes are selective to DHA, since it appears in some short reactions at low yields, as it is the first oxidation product that can be obtained. The formation of tartronic acid was also detected, enhancing the previous results.

Conclusions

A new gold(III) complex bearing Tpms (67% yield) coordinated in a bidentate fashion, directly from the commercially available metallic compound has been found and its structure confirmed by X-ray diffraction of a single crystal, contributing towards the still unexplored coordination chemistry of gold with C-scorpionate ligands.

The possibility of applying such complexes as catalyst precursors for oxidation under mild conditions of toluene, benzyl alcohol, glycerol and esterification of benzaldehyde under homogeneous conditions has also been opened.

The oxidation of toluene can be performed at 80 °C in the presence of nitric acid for 8 hours with complex **1**, or 6 hours with complex **2** achieving both nearly 8% of total yield with 82% of selectivity to benzaldehyde.

The oxidation of benzyl alcohol can be performed at 80 °C, with complex **1** achieving up to 42% higher yield, while complex **2** achieved up to 32% with a smaller amount of catalysts.

The esterification of benzaldehyde was successfully performed at room temperature for both catalysts. The quantity of methanol has an important influence on the reaction.

The use of complexes on the oxidation of sulphur compounds presents in diesel was not possible having, leaving room to investigate and improve the reaction and activity conditions.

The glycerol oxidation can also be improved.

The possibility of being able to use mild conditions for reactions that typically use harsh conditions is encouraging for the continued the research of gold complexes and their application in other reactions that follow the green chemistry principles.

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