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Aqueous-phase hydrogenation and hydroformylation reactions catalyzed by a new water-soluble [rhodium]–thioligand complex

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ABSTRACT

Rh(DHTANa) is a new water-soluble catalyst easily obtained by mixing in water the catalytic precursor $[Rh(COD)Cl]_2$ and the dihydrothioctic acid sodium salt (DHTANa). This catalyst showed to be very active in the hydrogenation of unsaturated substrates as 2-cyclohexen-1-one, the biomass-derived furfural and acetophenone. In this last case the catalytic system obtained by using as water-soluble ligand (R)-(DHTANa) afforded (R)-1-phenylethanol with very modest enantioselectivity. Rh(DHTANa) was active also in the aqueous biphase hydroformylation of styrene producing exclusively the two corresponding aldehydes with 80–86% selectivity toward the branched aldehyde 2-phenylpropanal. This new catalytic system was easily recycled in both hydrogenation and hydroformylation processes and no leaching phenomenon was observed.

1. Introduction

Homogeneous catalysis is an efficient tool to carry out a chemical process in a very active and selective way but the major drawback of the homogeneous process is the separation of the expensive catalyst from the product mixture that requires an energy intensive process such as distillation. In recent years the use of metallic species with suitable ligands has allowed chemists to carry out reactions in biphasic systems so permitting an easy separation of the used catalyst, confined in a phase different from that of reagents and products, and its re-use in recycling experiments; in particular, the use of both water as co-solvent for biphasic reactions and easily recyclable water-soluble catalysts are highly desirable for the realization of green processes [1–4]. In the last years natural compounds, such as aminoacids, peptides, proteins and sugars have been used as ligands for metallic species active as catalysts [5–9]. In this context, some years ago we reported highly efficient and chemoselective hydroformylation [10–12] and hydrogenation [8] reactions using water-soluble complexes derived from the interaction between $Rh(CO)_2(acac)$ or $[Ir(COD)Cl]_2$, respectively, with human serum albumin (HSA). Previous studies, carried out by us on the catalytic system Rh/HSA, showed an outstanding correspondence between the surface distribution of Rh and S atoms of the protein, therefore we hypothesized that the metal atom mainly interacts with the sulphur atoms [13,14]: the great affinity of "soft" metals, such as rhodium, for the thiolic group is well known [15]. As a matter of fact many rhodium complexes modified with thioligands have been successfully employed in catalytic reactions in homogeneous phase in organic solvents [16–23]. Our goal was to study catalytic processes in the presence of water-soluble sulphur containing ligands: in particular we used some thio-oligopeptides as ligands in the rhodium catalyzed hydroformylation of styrene [14]. More recently, we turned our attention to simple and cheap water-soluble low molecular weight thioligands such as the aminoacid L-Cysteine and [(S)-1-[(S)-3-mercapto-2-methylpropanoyl]pyrrolidine-2-carboxylic acid] (sold as a pharmacologically active ACE inhibitor, named Captopril®). Both ligands were capable of promoting efficiently the hydrogenation process in the presence of Rh or Ir catalytic precursors and, at the same time, allowing an easy recovery and recycling of the water-soluble catalytic complexes [24]. In these last months we addressed our research to the use of a very simple molecule, e.g. dihydrothioctic acid (DHTA), the reduced form of thioctic acid (THA), which presents two —SH groups capable, in principle, to work as a bidentate ligand for the rhodium atom (Fig. 1). The presence of another functional group, —COOH, in the molecule, when it is salified, might favor the solubility in water of the Rh complex but also create a potential third bonding site for the metallic species. Finally, as this molecule presents a chiral center and the corresponding enantiomers are easily prepared from a commercially

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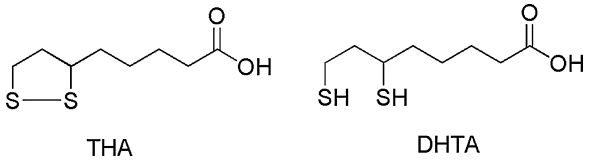

Fig. 1. Thioctic acid (THA) and dihydrothioctic acid (DHTA).

available enantiopure precursor, we could set out to evaluate the enantioselectivity in the hydrogenation of suitable substrates catalyzed by rhodium-(DHTA sodium salt) complex, from now on named Rh(DHTANa).

2. Experimental

2.1. Materials and methods

$[Rh(COD)Cl]_2$, 2-cyclohexen-1-one, furfural, acetophenone and styrene were Aldrich products. Thioctic acid and (R)-thioctic acid were a generous gift of Prochifar s.r.l. (Milan) and Sintactica s.r.l. Cassina De' Pecchi (Milan), respectively. GC analyses were carried out on an Agilent 6850 A gaschromatograph (HP1 column 30 m × 0.32 mm × 0.25 μm) and GC–MS analyses were performed by using an Agilent MS Network 5937 (HP-5MS column 30 m × 0.25 mm × 0.25 μm). Enantiomeric excess of 1-phenylethanol (**X**) was determined by GC equipped with a cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm thickness): initial T_{50} °C; initial t 1.1 min; solvent delay 4.48 min; T ramp 1.3 °C/min; final T_{150} °C. (R)-configuration was determined by polarimetric measurements by using a Perkin Elmer 241 polarimeter ($[\alpha]^{20}_D = +43$, c = 5 in CH_3OH for pure (R)-**X**). ICP-MS analysis was performed by using an Agilent 7500a-Series instrument.

2.2. Dihydrothioctic acid sodium salt (DHTANa) preparation

Dihydrothioctic acid (DHTA) was prepared as described [25].

Thioctic acid (510 mg, 2.5 mmol) was dissolved in a solution of 210 mg (2.5 mmol) of Na_2CO_3 in 12 mL of H_2O and cooled to 0 °C in an ice bath. $NaBH_4$ (190 mg, 5 mmol) was added slowly and the temperature kept below 4 °C while stirring for an additional 2 h. The reaction mixture was acidified with 2 M HCl to pH 1 and extracted with $CHCl_3$ (3 × 10 mL). The combined organic phases were dried over $MgSO_4$ and filtered. Evaporation of the solvent yielded 507 mg (98%) of DHTA as a clear colorless oil. The oil was maintained under nitrogen at low temperature (−20 °C). ^{1}HNMR ($CDCl_3$): δ 10.1 (bs, 1H, OH), 2.89 (m, 1H, S—CH), 2.7 (m, 2H, S—CH_2), 2.4 (t, J = 7.1 Hz, 2H, CH_2—COOH), 1.92–1.4 (m, 8H, $(CH_2)_4$), 1.36 (t, J = 7.9, 1H, SH), 1.31 (d, J = 7.6, 1H, SH). ^{13}C-NMR: δ 180.4 (COOH), 43.1 (SH—CH_2—**CH_2**—CH), 39.7 (**CH_2**—COOH), 39.1 (**CH_2**—CH—SH), 34.3 (CH—SH), 26.9 (CH—CH_2—**CH_2**), 24.7 (**CH_2**—CH_2—COOH), 22.7 (CH_2—SH). The corresponding sodium salt DHTANa was obtained by treatment of 507 mg (2.46 mmol) of DHTA with one equivalent of Na_2CO_3 dissolved in 10 mL of deaerated H_2O. ^{1}HNMR (H_2O/D_2O): δ 2.92 (m, 1H, S—CH), 2.6 (m, 2H, S—CH_2), 2.08 (t, J = 7.2 Hz, 2H, CH_2—COONa), 1.9–1.78 (m, 2H, $HSCH_2$**CH_2**CHSH), 1.72–1.3 (m, 10H, $(CH_2)_4$, 2 SH).

The aqueous solution obtained was then used for the preparation of the Rh(DHTANa) complex. In the same way (R)-(DHTANa) was prepared starting from (R)-thioctic acid.

2.3. Rh(DHTANa) catalyst preparation

The catalytic complex Rh(DHTANa) was prepared in situ by reacting, at room temperature under a nitrogen purge, $[Rh(COD)Cl]_2$ (12.4 mg, 0.025 mmol) with a solution of dihydrothioctic acid sodium salt (DHTANa) (10.3 mg, 0.5 mmol) in 5 ml of deaerated water until complete dissolution of the complex. ^{1}HNMR (H_2O/D_2O): δ 3.61 (m, 1H, S—CH), 3.12 (m, 2H, S—CH_2), 2.08 (t, J = 7.2 Hz, 2H, CH_2—COONa), 1.9–1.78 (m, 2H, $HSCH_2$**CH_2**CHSH), 1.72–1.3 (m, 10H, $(CH_2)_4$, 2 SH). By comparing the ^{1}HNMR of the free ligand DHTANa and the corresponding rhodium complex Rh(DHTANa) we can observe a clear shift of the protons present on the carbon atoms originally bound to the thiolic groups, so indicating a possible chelation of Rh to the S atoms.

In the same way (R)-Rh(DHTANa) was prepared starting from (R)-(DHTANa). The complex $Rh(DHTANa)_2$ was prepared at the above reaction conditions but by using a double amount of the water-soluble thioligand DHTANa.

2.4. Hydrogenation experiments

All reactions were carried out following the procedure below described for the hydrogenation of 2-cyclohexen-1-one (**I**). Experimental details for all the hydrogenations are reported in Tables 1–4.

2.4.1. Hydrogenation of 2-cyclohexen-1-one (*I*)

In a Schlenk tube, 1 mL of a 0.005 M solution of Rh(DHTANa) in deaerated water and 480 mg (5.0 mmol) of 2-cyclohexen-1-one (**I**) in 2 mL of deaerated H_2O were stirred under nitrogen. The Schlenk tube was then transferred into a 150 mL stainless steel autoclave under nitrogen, pressurized with H_2 and stirred for the due time at 60 °C (Table 2). The reactor was then cooled to room temperature and the residual gases released. Diethyl ether was added to the reaction mixture and the organic phase was separated, dried on Na_2SO_4 and analyzed by GC and GC–MS. The catalytic aqueous phase was recycled for further experiments after addition of fresh of 2-cyclohexen-1-one (**I**).

Table 1
Aqueous biphasic hydrogenation of cycloehex-2-en-1-one (**I**) catalyzed by Rh(DHTANa).

Run	Sub/cat. (molar ratio)	t (h)	Conv. (%)	**II** yield (%)	**III** yield (%)	**IV** yield (%)	TOF[a]
1	500	4	99	95	4	nd	124
2[b]	500	4	99	90	9	nd	124
3[b]	500	4	99	93	6	nd	124
4[b]	500	4	84	82	2	nd	105
5	1000	4	69	68	1	nd	173
6[b]	1000	4	69	68	1	nd	173
7[b]	1000	4	55	54	1	nd	138
8	1000	6	99	96	3	nd	165
9[b]	1000	6	99	97	2	nd	165
10[b]	1000	6	99	97	2	nd	165

Substrate = 5 mmol; T = 60 °C; p(H_2) = 2 MPa; H_2O = 2 ml; toluene = 1 ml. nd = not detected in the reaction mixture.
[a] TOF = (mol **I**/mol cat.)h^{-1}.
[b] Experiment carried out by using the catalytic phase recovered from the previous run.