

Synthesis, characterization and aqueous-biphasic catalysis of the ruthenium dimer



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Abstract

The dimer $\text{Na}[\{\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\text{Ru}\}_2(\mu\text{-Cl})_3] \cdot 3\text{H}_2\text{O}$ has been synthesized by the reaction of the tripodal ligand $\text{NaO}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$ with the ruthenium complex $[\text{RuCl}_2(\text{DMSO})_4]$. The dimeric complex is an effective catalyst precursor for the liquid-biphasic hydrogenation of the double bond in various alkenes (1-hexene, 1-decene, allylbenzene, styrene) as well as the heteroaromatic ring in benzo[*b*]thiophene and quinoline. All the metal remains in the polar phase at the end of the catalytic reactions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous-biphasic catalysis; Hydrogenation; Ruthenium; Hydrodesulfurization; Hydrodenitrogenation

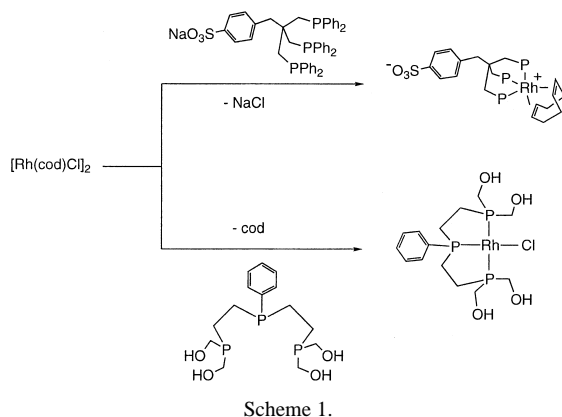
1. Introduction

Catalysis in water or in aqueous-biphasic systems is emerging as the technique of the future for the production of commodities, specialties and fine chemicals [1,2]. Increasing research efforts are being paid to the design of appropriate water-soluble ligands among which tertiary phosphines play a major role in terms of both versatility of coordination and industrial application [1–3]. In an attempt to combine high

catalytic activity with high selectivity, research aimed at synthesizing water-soluble metal complexes containing tridentate phosphines has greatly expanded over the last two years. Two different strategies have been developed to design water-soluble tridentate phosphines as illustrated by the ligands $\text{NaO}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$ (NaSulphos) and $\text{PhP}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{OH})_2]_2$ recently described by Bianchini et al. [4] and Smith et al. [5], respectively (Scheme 1). In the ligand NaSulphos, the polar group is far away from the phosphorus donors. Accordingly, these maintain the electronic and steric properties of the $-\text{PPh}_2$ groups which are commonly encountered in highly active phosphine-promoted metal catalysts. Due to its tripodal structure, NaSulphos coordinates metal cen-

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tres exclusively in a *facial* geometry [4]. In contrast, the linear triphosphine $\text{PhP}[\text{CH}_2\text{P}(\text{CH}_2\text{OH})_2]_2$ can bind transition metals in either *facial* or *meridional* arrangement, and the CH_2OH substituents may compete with the phosphorus donors for coordination, particularly towards oxophilic metal ions. A unique and highly positive characteristic of $\text{PhP}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{OH})_2]_2$ is the different basicity of the bridgehead PPh and terminal $\text{P}(\text{CH}_2\text{OH})_2$ groups. This feature may be useful for the development of transition-metal complexes in which the weaker of the two different M–P bonds may be reversibly cleaved during a catalytic cycle depending on the formal oxidation state of the metal centre. Various metal complexes with these tridentate ligands have been prepared and characterized as is exemplified in Scheme 1 for the zwitterionic five-coordinate Rh(I) derivative $[\text{Rh}(\text{cod})(\text{Sulphos})]$ (cod = cycloocta-1,5-diene) and the square-planar complex $[\text{RhCl}\{\text{PhPCH}_2\text{CH}_2\text{P}(\text{CH}_2\text{OH})_2\}_2]$. Catalytic reactions in liquid-biphase systems have exclusively been reported for Sulphos complexes, however [4,6,7]. In particular, $[\text{Rh}(\text{cod})(\text{Sulphos})]$ behaves as an effective catalyst precursor for the hydrogenation and hydroformylation of alkenes [4] as well as the hydrogenation and hydrogenolysis of benzo[*b*]thiophene to 2,3-dihydrobenzo[*b*]thiophene and 2-ethylthiophenol, respectively [6].

The promising results obtained with rhodium prompted us to explore the coordination chemistry of NaSulphos towards other transition metals with potential in aqueous-biphase catalysis. In this work, we report the synthesis and characterization of the ruthenium(II) dimer $\text{Na}[\{\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\text{Ru}\}_2(\mu\text{-Cl})_3 \cdot 3\text{H}_2\text{O}(\mathbf{1})$. A brief account of the catalytic activity of **1** in the hydrogenation of various alkenes (1-hexene, 1-decene, allylbenzene, styrene) and of aromatic heterocycles (quinoline, benzo[*b*]thiophene) in H_2O – MeOH –*n*-heptane is also reported. The latter two substrates are well-known contaminants of fossil fuels from which they are currently removed by hydrogenation over heterogeneous catalysts (hydrodenitrogenation and hydrodesulfurization processes [8]).

2. Experimental section

2.1. Experimental procedure

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were dried and deoxygenated prior to use. The ligand NaSulphos [4] and the complex $[\text{RuCl}_2(\text{DMSO})_4]$ [9] were prepared according to literature procedures. High-pressure, high-temperature reactions under a controlled pressure of H_2 were performed with a stainless steel 300 ml Parr reactor. Cs FABMS analyses were carried out using a VG-ZAB.2SEQ mass spectrometer (*m*-nitrobenzyl alcohol, matrix) at 35 kV and at a mass resolution high enough to resolve peaks at one mass unit apart. GC-MS analyses were performed with an HP 5890 system, HP-1 column, 50 m; split injection of 1:50. GC chromatograms were run on a Varian 3400 with a FI detector (Megabore type capillary column, 15 m; DB-5 phase; 1.5 μ FT, J&W Scientific). Quantification was achieved by using the internal standard method. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker 200 or 400 MHz spectrometers, using deuterated solvents. All chemical shifts are reported in parts per

million (δ) relative to tetramethylsilane (^1H) or 85% H_3PO_4 (^{31}P). Elemental analyses (C, H) were performed using a Carlo Erba Model 1106 elemental analyzer. The quantitative determination of chlorine was obtained by standard gravimetric procedures. Atomic absorption analyses were performed with a Perkin Elmer 5000 instrument.

2.2. Synthesis of $\text{Na}[\{\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}-(\text{CH}_2\text{PPh}_2)_3\text{Ru}\}_2(\mu\text{-Cl})_3] \cdot 3\text{H}_2\text{O}$ (**1**)

The complex $[\text{RuCl}_2(\text{DMSO})_4]$ (200 mg, 0.413 mmol) and the ligand NaSulphos (332 mg, 0.413 mmol) in 30 ml of toluene were placed into a 100 ml round-bottomed flask. The resulting slurry was stirred for 16 h at 90°C. After cooling to room temperature, the yellow powder, which had separated, was filtered off, washed with toluene and diethyl ether and then dried in vacuo. Yield: 0.345 g, (89%). Complex **1** is air-stable and soluble in DMSO, MeOH, DMF, acetone and in hot water/methanol mixtures (1:1, v:v) where it is thermally stable up to 140°C. Anal. Calcd. for $\text{C}_{94}\text{H}_{90}\text{Cl}_3\text{NaO}_9\text{P}_6\text{Ru}_2\text{S}_2$ ($M = 1945.08$): C, 58.04; H, 4.35; Cl, 5.56. Found: C, 57.91; H, 4.34; Cl, 5.17. $^{31}\text{P}\{^1\text{H}\}$ NMR (20°C, $\text{DMSO}-d_6$): δ 35.77, s. ^1H NMR (20°C, $\text{DMSO}-d_6$): δ 2.64, br, 12H (CH_2P); 3.30, s, 4H ($\text{C}_6\text{H}_4\text{CH}_2\text{C}$); 7.80, d, 8 Hz, 4H (*m*-H of $\text{O}_3\text{SC}_6\text{H}_4$); 7.66, d, 8 Hz, 4H (*o*-H of $\text{O}_3\text{SC}_6\text{H}_4$); 7.39, br s, 24 H (*o*-H of PPh_2); 7.27, t, 7 Hz, 12H (*p*-H of PPh_2); 6.91, t, 7 Hz, 24 H (*m*-H of PPh_2). IR (Nujol mulls): 1191 cm^{-1} , br, m, $-\text{SO}_3$. FABMS: calcd. for $\text{C}_{94}\text{H}_{84}\text{Cl}_3\text{NaO}_6\text{P}_6\text{Ru}_2\text{S}_2$, m/z 1891. Found: peaks centered at 1892, 1870, 1790, 917 m/z which, on the basis of the isotopic distribution of the elements, particularly of ruthenium, are assigned to the ions $[\text{M}]^+$, $[\text{M}-\text{Na}]^+$, $[\text{M}-\text{Na}-\text{HSO}_3]^+$, and $[(\text{Sulphos})\text{RuCl}]^+$, respectively.

2.3. Catalytic runs

In a 300 ml stainless steel vessel of a Parr autoclave containing 70 ml of a deaerated 3:2:5

mixture of water/methanol/*n*-heptane were placed **1** (0.05 mmol), the substrate (5.0 mmol) and 2-methylnaphthalene (2.5 mmol) as the internal standard. After pressurizing with 30 atm of H_2 , the reactor was heated to 140°C with stirring (600 rpm). After the desired time, the reactor was cooled to room temperature and the two phases were separated. The colourless organic phase was analyzed by GC and GC-MS. After all the organic solvent was removed under reduced pressure, the residue was analyzed by atomic absorption which showed the absence of ruthenium in the residue.

3. Results and discussion

The dimer **1** is straightforwardly obtained as yellow microcrystals by reacting $[\text{RuCl}_2(\text{DMSO})_4]$ with an equivalent amount of the tripodal ligand NaSulphos in warm toluene. The water molecules can be removed from **1** upon prolonged heating to 100°C under reduced pressure. The dry compound picks up water from the environment quite rapidly, however. The compound is soluble in polar solvents, including methanol–water mixtures. The solubility in water is too low, however, to employ this complex in water catalysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** consists of a temperature-invariant singlet at δ 35.77 in $\text{DMSO}-d_6$ (δ 34.29 in $\text{MeOH}-d_4$ and 33.92 in $\text{DMF}-d_7$) and is quite coincident with the spectrum of the derivative $[\text{Ru}_2(\mu\text{-Cl})_3\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}_2][\text{BPh}_4]$ reported by Venanzi et al. (singlet at 36 ppm in CD_2Cl_2) for which an X-ray structural analysis is also available (Fig. 1) [10].

On the basis of the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR, IR and FABMS spectra, **1** is safely assigned a

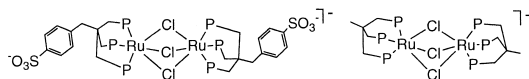


Fig. 1. Sketches of the dimeric Ru(II) complex ions with Sulphos and triphos.

structure in which two ruthenium(II) centres are held together by three chloride bridges. A sodium counterion assures the compound of electroneutrality. The formation of dimers containing a triple chloride bridge and three terminal phosphine ligands is quite common for ruthenium [10–12]. However, Complex **1** is the first derivative which is soluble in aqueous mixtures.

The activity of **1** as catalyst precursor for the liquid-biphasic hydrogenation of various hydrophobic alkenes was investigated at 140°C and 30 atm of H₂ in a 3:2:5 mixture of water/methanol/*n*-heptane (Table 1). The reactions do not require the addition of a surfactant, which is consistent with the inherent emulsifying properties of Sulphos complexes [4,6,7]. In these experimental conditions, **1** is capable of catalyzing the hydrogenation of 100 equiv of 1-hexene, 1-decene and allylbenzene almost completely in 1 h. In the case of 1-hexene and 1-decene, appreciable isomerization (3%) is also observed, while allylbenzene is selectively converted to propylbenzene. Styrene is the hardest substrate to hydrogenate as its total conversion to ethylbenzene requires a reaction time of 5 h. At the end of each catalytic run, an efficient separation of the two phases is achieved to give a colourless organic phase exclusively containing the organic products. No appreciable trace of ruthenium species was detected by atomic absorption analysis of the solid residue after the

Table 1
Alkene hydrogenation reactions catalyzed by **1**^a

Substrate (% conversion)	Product (% selectivity)
1-Hexene (100)	<i>n</i> -Hexane (97) ^b
1-Decene (100)	<i>n</i> -Decane (97) ^c
Styrene (27)	Ethylbenzene (100)
Allylbenzene (100)	Propylbenzene (100)

^aConditions: 140°C, 30 atm H₂, substrate to catalyst ratio = 100, 1 h, mixture of methanol (20 ml), water (30 ml) and *n*-heptane (50 ml).

^bThe remaining 3% comprises *cis*- and *trans*-2-hexene, and *cis*- and *trans*-3-hexene.

^cThe remaining 3% comprises *cis*- and *trans*-2-decene, 3-decene, 4-decene and 5-decene.

Table 2
Hydrogenation reactions of benzo[*b*]thiophene and quinoline catalyzed by **1**^a

Substrate (% conversion)	Product (% selectivity)
Benzo[<i>b</i>]thiophene (94)	2,3-Dihydrobenzo[<i>b</i>]thiophene (100)
Quinoline (95)	1,2,3,4-Tetrahydroquinoline (100)

^aConditions: 140°C, 30 atm H₂, substrate to catalyst ratio = 100, 3 h, mixture of methanol (20 ml), water (30 ml) and *n*-heptane (50 ml).

organic solvent was eliminated under reduced pressure.

The dimer **1** is an effective biphasic catalyst precursor for the selective hydrogenation of benzo[*b*]thiophene to 2,3-dihydrobenzo[*b*]thiophene and of quinoline to 1,2,3,4-tetrahydroquinoline (Table 2). No product derived from the cleavage of C–S or C–N bonds in either substrate was observed. The appreciable solubility of quinoline and 1,2,3,4-tetrahydroquinoline in water causes a 20% loss of nitrogen in the mass balance as determined by quantitative GC analysis of the organic phase.

The catalytic profiles of the hydrogenation reactions of all substrates are illustrated in Fig. 2. From a perusal of the results obtained, one may readily infer that the catalytic activity of **1** decreases in the order: 1-hexene = 1-decene = allylbenzene > quinoline = benzo[*b*]thiophene > styrene. The fact that styrene is the hardest alkene to hydrogenate is in line with the large steric hindrance at the metal centre in complexes containing Sulphos [6] or similar tripodal triphosphine ligands [13]. Consistently, 1-hexene and 1-decene are hydrogenated at comparable rates, which is particularly surprising for the very hydrophobic 1-decene substrate in the absence of a surfactant.

Hydrogenation reactions of alkenes in two-phase systems by water-soluble ruthenium complexes have already been reported in the literature [1–3]. The present example represents the first of such reactions in which a dimeric ruthenium complex is employed as catalyst precursor. However, this does not mean that the cata-

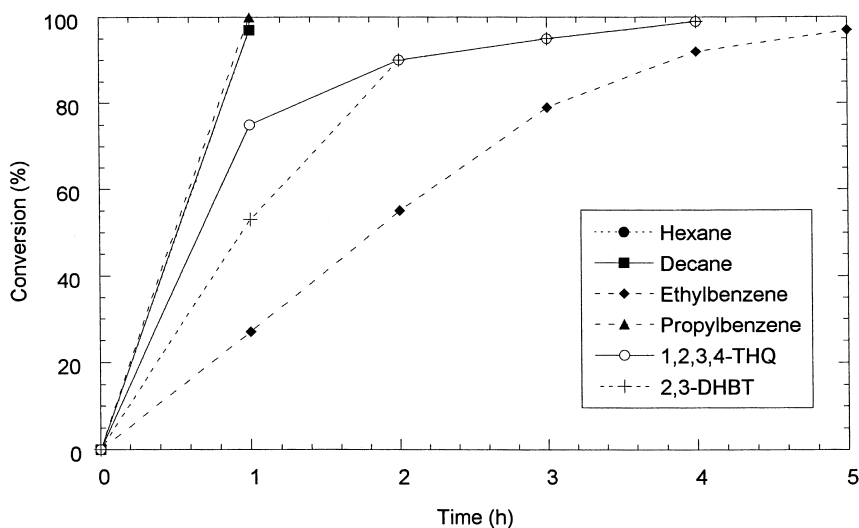


Fig. 2. Profiles (conversion vs. time) of the hydrogenation reactions of different substrates catalyzed by **1**.

lytically active species necessarily maintains the dimeric structure.

Finally, it is worth highlighting the good hydrogenating activity exhibited by **1** towards quinoline and benzo[*b*]thiophene. To the best of our knowledge, only one previous example of Ru-assisted aqueous-biphase hydrogenation of these two heteroaromatic substrates has been reported so far. The known example involves a catalytic system generated in situ by addition of either *m*-monosulphonated triphenylphosphine or trisulphonated triphenylphosphine to various Ru(II) and Ru(III) precursors in a 1:1 water/decaline mixture [14]. The hydrogenation rates of both substrates are comparable to those found for the catalyst precursor **1**.

4. Conclusions

The dimer $\text{Na}[\{\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{-PPh}_2)_3\text{Ru}\}_2(\mu\text{-Cl})_3] \cdot 3\text{H}_2\text{O}$ behaves as an effective catalyst precursor for the aqueous-biphase hydrogenation of C–C double bonds of α -olefins and of the heteroaromatic ring of quinoline and benzo[*b*]thiophene water/methanol/*n*-heptane mixture under moderate reaction conditions. The liquid-biphase character of the

reactions allows one to easily separate the catalyst from the products.

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