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Catalytic activity of $RuCl_2(DMSO)_4$ in biphasic and homogeneous systems

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Water soluble $RuCl_2(DMSO)_4$ is an active catalyst precursor for 1-hexene hydrogenation in water/organic solvent biphasic systems, reaching 98% total conversion (400 psi H_2, 80 °C, 6 h), with n-hexane as the principal product and less of the 2-hexene isomers, favoring *cis*-2-hexene. It is very sensitive to O_2 dissolved in water, and decomposes when halide salts or alcohols are added. The Ru complex is also active in an alcohol homogeneous phase, but less than in the biphasic system, gives a greater isomer proportion, favoring *cis*-2-hexene and increases with potassium halide salt additives.

Keywords: hydrogenation and isomerization reactions, biphasic catalytic system, ruthenium complexes, DMSO complexes, halide salt promoters

1. Introduction

There is great interest in complexes with water soluble ligands and their use in biphasic reaction catalysis [1,2]. $RuCl_2(DMSO)_4$, (**1**), is used in the synthesis of other Ru complexes taking advantage of DMSO ligand lability [3], but its catalytic activity has not been thoroughly studied. Catalytic water soluble ruthenium complexes have been reported with sulphonated phenyl phosphine ligands ($Ph_2P(m\text{-}C_6H_4SO_3Na)$, L^1, and $P(m\text{-}C_6H_4SO_3Na)_3$, L^3). $HRu(OOCH_3)(L^1)_3$, $RuCl_2(L^1)_2$, or $HRuCl(L^1)_3$ are active in the hydrogenation of 2-ketoacids [4(a)], hydrogenation of 1-hexene, *cis/trans* 2-hexene [4(b),5] styrene [4(b)] and cyclohexene [5], hydrogenation of *trans*-2-butendioic acid [4(c)], hydrogenation of unsaturated aldehydes [4(d)], conversion of aldehydes to alcohols [6(a),(b)], hydroformylation of 1-hexene [5] and hydrogenation of piruvic acid [4(b)]. $HRuI(L^3)_2$ is formed *in situ* with NaI promoter in catalytic reactions [7]. Ru-EDTA hydrogenates unsaturated substrates [8(a),(b)]. In this work, the hydrogenation activity of (**1**) in biphasic systems is presented and compared with homogeneous reactions in alcohol.

2. Experimental

2.1. Synthesis

Complex (**1**) was synthesized using $RuCl_3{\cdot}3H_2O$ (Strem Chemical) and characterized by IR (KBr, Perkin–Elmer 1725-X FTIR) [3] (ν(CH) 3020(s) and 3009(s) cm^{-1}, ν(S bonded) 1120(s) and 1095(s) cm^{-1}; ν(CS) 628(m) cm^{-1}). All solvents used are dried under inert atmosphere. Liquid olefins (Aldrich Chemical) and gases (H_2, Ar, AGA) are used directly.

2.2. Catalytic reactions

2.2.1. Biphasic system

In a typical experiment, complex (**1**) (3 mg, 6.2×10^{-3} mmol) in 2 ml of thoroughly deoxygenated distilled water (aqueous phase) plus 2 ml of olefin (e.g., 1-hexene, 16 mmol, organic phase; substrate/catalyst molar ratio $=$ 2585) are placed in the 10 ml glass liner of a high-pressure reactor (10 ml, Parr Instr. Co, Aschcroft 5000 psi manometer) under Ar with magnetic stirring. The reactor is purged three times with H_2, filled to the desired pressure and heated to the selected temperature with a paraffin bath, allowing 5 min for thermal stabilization. The reactor is cooled rapidly when the reaction ends, the two phases separated and analyzed by gas chromatography (CG Perkin–Elmer AutoSystem 900, FID and TCD detectors; 15% tricresyl phosphate over Chromosorb P column, 60–80 mesh, 3 m long, 0.6 cm diameter, stainless steel). The biphasic system is particularly O_2 sensitive and must be carefully excluded; a similar problem has been reported for Ru water soluble complexes [4(b)].

2.2.2. Homogeneous system

The method and the analysis are similar to the biphasic system, but 2 ml of freshly purified alcohol are used instead of water.

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3. Results and discussion

3.1. Biphasic system: water/1-hexene. H_2 pressure dependence

The results are shown in figure 1 (reaction conditions: 6 h, 80 °C, substrate/catalyst molar ratio = 2585). The saturated alkane is favored at higher H_2 pressures compared with the internal isomers with greater than 90% conversion at 1200 psi. The isomers are favored at lower than 200 psi H_2 pressures, with greater selectivity to *cis*-2-hexene, favoring the kinetic product over the thermodynamic mixture suggesting an important steric requirement. The internal isomers are hydrogenated to the alkane at high H_2 pressures at a slower rate than 1-hexene.

3.1.1. Temperature dependence

The results are shown in figure 2 (reaction conditions: 4 h, 400 psi H_2; substrate/catalyst molar ratio = 2585). There is no catalytic activity at 20 °C; the hydrogenation product increases rapidly at higher temperatures, and in lesser amounts the isomerization products; the ruthenium complex is unstable at temperatures higher than 85 °C.

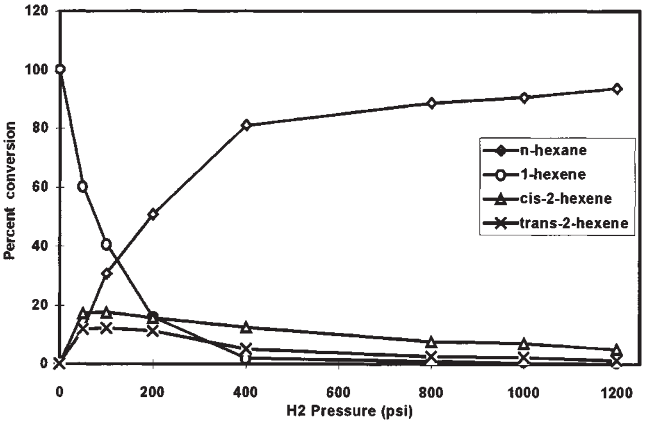

Figure 1. Biphasic system: H_2 pressure dependence. Reaction conditions: 6 h, 80 °C, substrate/catalyst molar ratio = 2585.

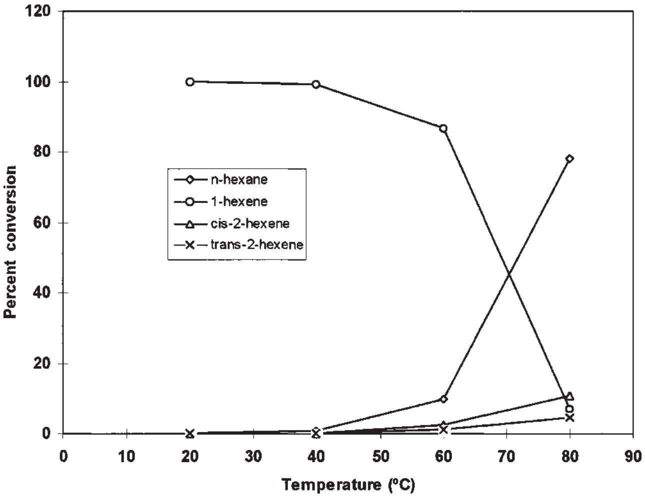

Figure 2. Biphasic system: temperature dependence. Reaction conditions: 4 h, 400 psi H_2; substrate/catalyst molar ratio = 2585.

3.1.2. Reaction time dependence

The results are shown in figure 3 (reaction conditions: 400 psi H_2, 80 °C; substrate/catalyst molar ratio = 2585). n-hexane production increases gradually with reaction time and levels off after 4 h as 1-hexene is consumed; isomer production increases slowly during reaction time and all the 1-hexene has been converted to products after 6 h.

3.1.3. Substrate/catalyst molar ratio dependence

The results are shown in table 1(a) (reaction conditions: 2 h, 400 psi H_2, 80 °C). Percent conversion mainly to the alkane increases as the substrate/catalyst molar ratio decreases (greater relative amount of catalyst). No products are observed in the absence of (**1**) under the same reaction conditions.

3.1.4. Cosolvent and additives dependence

The results for the cosolvents are shown in table 1(b) (reaction conditions: 4 h, 400 psi H_2, 80 °C, substrate/catalyst molar ratio = 2585; methanol : water (= 1 : excess, 1 : 1, 1 : 2, 2 : 1 and excess : 1). Total percent conversion is drastically reduced when an alcohol (2-propanol, butanol,

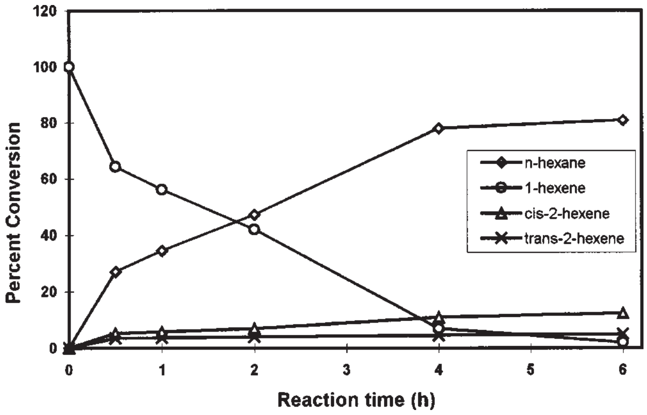

Figure 3. Biphasic system: reaction time dependence. Reaction conditions: 400 psi H_2, 80 °C; substrate/catalyst molar ratio = 2585).

Table 1

Biphasic system: (a) dependence with substrate/catalyst molar ratio and (b) dependence on cosolvents used (%).

	1-hexene	n-hexane	*Cis*-2-hexene	*Trans*-2-hexene
(a) Molar ratio				
7755	58.5	32.3	5.5	3.7
2585	41.9	47.2	6.9	4
1292	32.4	55.6	7.8	4.2
861	24.3	62.3	8.9	4.5
(b) Cosolvent				
Water	6.9	77.8	10.8	4.5
2-propanol	83.4	10.2	4.2	2.2
Butanol	88.6	6.8	3.1	1.5
Ethanol	92	4.3	2.8	0.9
Methanol	94.4	2.4	2.5	0.7

ethanol, methanol) is added to the water/1-hexene mixture. Alcohol as a cosolvent modifies the catalytic biphasic reaction by changing substrate or catalyst solubility in one of the liquid phases, or changes the interface surface tension. The notable percent conversion reduction observed with alcohols as cosolvents was unexpected, since no noticeable solubility changes are observed for (**1**) in the water–alcohol mixtures. Iodide salts [9], NH_4PF_6, NH_4BF_4 [10], PPNCl ($N(PPh_3)_2Cl$), $N(n\text{-butyl})_4Cl$ [11] were tried as catalytic promoters for the biphasic reaction, but the results observed at 20 °C and moderate temperatures indicated that the organometallic system is unstable, leading to important decomposition.

3.1.5. Reutilization of the ruthenium complex (water phase)

The results are shown in table 2 (reaction conditions: 4 h, 400 psi H_2, 80 °C, substrate/catalyst molar ratio = 2585). A 30% decrease in activity is noticed after two reuses and is reduced to 15% after four reutilizations due to catalyst decomposition during the separation process. Hydrogenation to n-hexane is reduced faster than isomer production.

3.1.6. Hydrogenation of other unsaturated substrates

The reaction of 1-pentene (reaction conditions: 1000 psi H_2; 2 h; 80 °C; substrate/catalyst molar ratio = 2808) is similar to that observed for 1-hexene, favoring the hydrogenation product (38.3%) and smaller amounts of the internal isomers (4.7%). 1-hexyne (reaction conditions: 1000 psi H_2; 5 h; 80 °C; substrate/catalyst molar ratio = 2953) gets hydrogenated more slowly and under stronger conditions, as is expected for carbon–carbon triple bonds (n-hexane 0.6% and 1-hexene 2.2%).

Table 2
Biphasic system: reutilization of the Ru complex water solution (%).

Number of reuses	1-hexene	n-hexane	*Cis*-2-hexene	*Trans*-2-hexene
1	6.9	77.8	10.8	4.5
2	35.2	55.3	6.5	3
3	71.9	21.4	4.5	2.2
4	83.9	10.1	4.1	1.9

3.2. Catalytic activity of $RuCl_2(DMSO)_4$ in homogeneous system

Similar conditions to the biphasic system were used (400 psi H_2, 80 °C, 4 h; substrate/catalyst molar ratio = 2585; 2 ml solvent).

3.2.1. Solvent dependence

The results are shown in figure 4. The homogeneous system gives good total percent conversion in the order: ethanol (69.4%) > methanol (51.9%) > 2-propanol (35%). The total percent conversion in the homogeneous system is smaller than in the biphasic system (93.1%). In all the homogeneous cases there is a greater relative proportion of internal isomers compared with the hydrogenation reaction, with better selectivity for the *cis*-2-hexene isomer and the best proportion obtained in methanol.

3.2.2. Dependence with KX promoter addition

Reaction conditions: 400 psi H_2, 80 °C, 4 h; substrate/catalyst molar ratio = 2585; 2 ml solvent, 2.5 mg. KX, X = Cl, Br, I. The results are shown in table 3. In ethanol total conversion remains similar to the system without promoter, but hydrogenation to alkane is favored. In methanol, isomerization to *cis*-2-hexene is notably favored and total conversion is increased; there are small variations depending on the potassium halide salt used, with better selectivity to *cis*-2-hexene with chloride and iodide salts. These results indicate that the halide ion participates in the

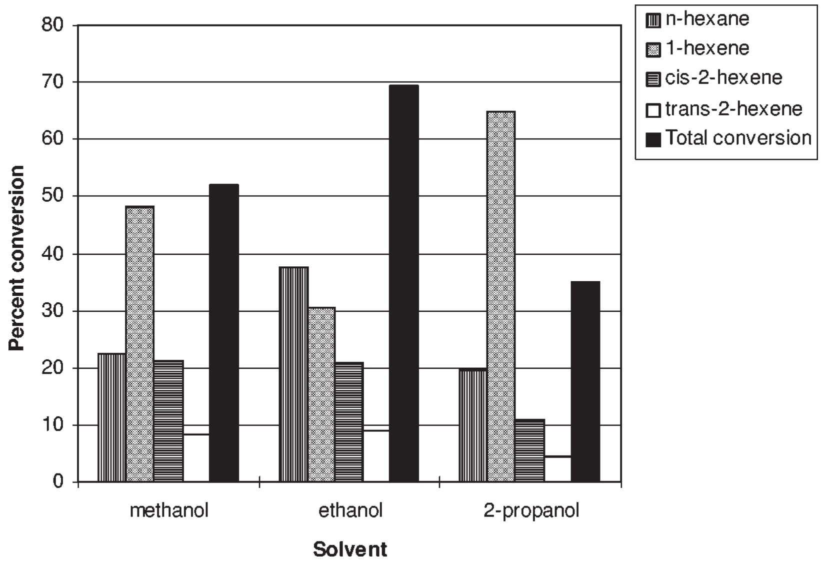

Figure 4. Homogeneous system: solvent dependence. Reaction conditions: 400 psi H_2, 80 °C, 4 h; substrate/catalyst molar ratio = 2585; 2 ml solvent.

Table 3
Homogeneous system: dependence with KX promoter (%).

Solvent–KX	1-hexene	n-hexane	*Cis*-2-hexene	*Trans*-2-hexene	Total conversion
Ethanol–KI	30.9	46.3	14.6	8.2	69.1
Methanol–KI	8.8	24.9	47.1	19.2	91.2
Methanol–KCl	4.1	29.4	48.2	18.3	95.9
Methanol–KBr	4.8	39.9	40.3	15	95.2

catalytic cycle, most likely as a labile ligand associated with the ruthenium complex.

4. Conclusions

$RuCl_2(DMSO)_4$ is an appropriate catalyst precursor for 1-hexene hydrogenation in a water/organic solvent biphasic system at moderate reaction conditions, is selective for the linear alkane and shows smaller amounts of the internal isomers. The hydrogenation process increases at higher H_2 pressures ($>$800 psi); temperature control is a critical factor, since there is a small temperature window ($\sim$60–85 °C) for system stability. The kinetic *cis*-2-hexene isomer is favored over the thermodynamic *trans*-2-hexene isomer, indicating some important steric requirements in the catalytic cycle. The biphasic system is destabilized with addition of alcohols and ionic promoters, even at low temperatures. $RuCl_2(DMSO)_4$ in a homogeneous system shows less total conversion than the biphasic system, but greater isomer percent conversion. Homogeneous catalytic activity improves notably with potassium halide addition, especially isomerization products with selectivity to *cis*-2-hexene over *trans*-2-hexene.

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