



## Olefin hydroformylation catalysis with $\text{RuCl}_2(\text{DMSO})_4$ .

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### Resumen:

El complejo  $\text{RuCl}_2(\text{DMSO})_4$  se usó como precursor catalítico en reacciones de hidroformilación de olefinas, dando buen porcentaje de conversión y mejor selectividad hacia aldehídos lineales. Las reacciones fueron probadas en medio homogéneo y en sistemas bifásicos solvente orgánico/ agua. Los sustratos probados fueron 1-hexeno, ciclohexeno, 2-metil-2-penteno, 2,3 dimetil-2-buteno; mezclas binarias, nafta sintética y nafta real. La actividad es mejor para olefinas lineales comparada con olefinas sustituidas.

**Palabras clave:** reacción de hidroformilación; olefinas; complejos de rutenio solubles en agua; reacciones bifásicas.

### Abstract

The  $\text{RuCl}_2(\text{DMSO})_4$  complex was used as catalytic precursor in olefin hydroformylation reactions, giving good percent yield and better selectivity for linear aldehydes. The reactions were tested in homogeneous medium and biphasic organic solvent/ water systems. The substrates tried were 1-hexene, cyclohexene, 2-methyl-2-pentene, 2,3-dimethyl-2-butene; binary mixtures and synthetic naphtha and real naphtha. The activity is better for linear olefins compared with substituted olefins.

**Key words:** hydroformylation reactions; olefin; water soluble ruthenium complexes; biphasic reactions.

### Introducción

The use of homogeneous catalysts in industrial processes is limited mainly due to separation difficulties of the products and metal catalyst, and the latter usually cannot be recovered<sup>1</sup>. In many industrial chemical processes, biphasic systems have been incorporated in linear and cyclic olefin hydroformylation to give aldehydes and alcohols. In biphasic catalysis, the use of water soluble ligands that make the metal catalyst water soluble has been increasing, as is the case with tri-sulphonated-triphenyl phosphine ( $\text{P}(\text{m-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ ; TPPTS)<sup>2</sup>. The biphasic system organic solvent/ water is one of the most used in laboratory and industrial catalysis<sup>3,4</sup>. In our laboratory we have used the TPPTS and DMSO ligands with water soluble Ru catalysts in different biphasic processes<sup>5-10</sup>. There have been several studies using real naphtha as a substrate in hydroformylation and hydrogenation processes as a general strategy for fuel improvement<sup>11-17</sup>. In this article we report olefin hydroformylation with the water soluble  $\text{RuCl}_2(\text{DMSO})_4$  complex.

### Experimental

**Reagents and Materials:**  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , DMSO, 1-hexene, cyclohexene, 2-methyl-2-pentene, 2,3-dimethyl-2-butene (Aldrich Chem. Co.); toluene, absolute ethanol (Riedel-Haen); Ar, CO, H<sub>2</sub>, air (Gases Industriales de Venezuela). All reactions are carried out under Ar. All solvents were distilled under Ar before use. The infrared spectra were taken in a Perkin Elmer 1600 FTIR (KBr pellets; 4000 - 400  $\text{cm}^{-1}$  range). The hydroformylation reactions were carried out in a high pressure batch reactor (Parr Instruments, 10  $\text{cm}^3$ , 2500 psi maximum pressure; glass liner, internal magnetic stirrer, temperature control); hydroformylation products were analyzed in a Perkin-Elmer Autosystem GC 900, with FID detector (methyl silicone Quadrex column, 50 m. long, 0,52 cm diameter).  $\text{RuCl}_2(\text{DMSO})_4$  was synthesized by the Evans, Wilkinson method<sup>18</sup>, with the modifications proposed by Alessio *et al.*<sup>19,20</sup>.

## Results and discussions

### 1. Catalytic hydroformylation trials of model compounds:

#### 1.1.- 1-hexene:

A) Homogeneous phase: Reaction conditions: Solvent (Toluene, 2 mL); substrate (1-hexene, 2 mL); RuCl<sub>2</sub>(DMSO)<sub>4</sub> (4 mg); substrate/ catalyst ratio: 600:1; Temperature: 100 °C; Total pressure: 1000 psi; CO/H<sub>2</sub>: 1:1; reaction time: 24 hr.

The hydroformylation results are shown in Table 1. The total % conversion is high, the OXO reaction favors the linear aldehyde, but a large proportion of aldehyde in the 2-position is produced, and the competing reaction to the *cis* and *trans* isomerization products is also observed.

B) Biphasic reaction: Reaction conditions: Solvent (Toluene or cyclohexane; 2 mL); water (2 mL); substrate (1-hexene, 2 mL); RuCl<sub>2</sub>(DMSO)<sub>4</sub> (15 mg or 4 mg); substrate/ catalyst ratio: 600:1; Temperature: 100 °C; Total

pressure: 1000 psi; CO/H<sub>2</sub>: 1:1 and 3:1; reaction time: 24 hr.

The hydroformylation results are shown in Table 2. The results with a CO/H<sub>2</sub> 1:1 ratio, are similar to the homogeneous phase results, with an important isomerization production. With an increase in the CO/H<sub>2</sub> ratio to 3:1, the percent conversion is reduced, mainly due to a reduction in the OXO reaction, since the isomerization reaction remains at about the same level. This could be due to inhibition in the catalytic reaction with the increase in CO pressure, since the CO is a good ligand and could compete for the coordination sites in the catalytic species. When the organic phase is changed to cyclohexane, the percent conversion remains high, mainly to OXO products and the isomerization competing reaction is very low.

One aspect that is observed both in the toluene and cyclohexane solvents, is the in situ production of a

**Table 1.** 1-hexene hydroformylation products in homogeneous phase

Compound	Conversion (%)	Products (%)	Selectivity* (%)
1-hexene	99	Ethyl pentanal (3)	Oxo products (58)
		Methyl-hexanal (20)	
		Heptanal (35)	Isomerization (41)
		Cis+ trans 2-hexene (41)	

\*Selectivity=  $(n_i / \sum n_i) \times 100$ ;  $n_i$  = mmols of product  $i$ ;  $\sum n_i$  = sum of all products measured as GC areas.

**Table 2.** Hydroformylation of model compounds – biphasic reaction

Compound	Conversion (%)	Products (%)	Selectivity* (%)
1-hexene (Toluene/ water) (CO/H <sub>2</sub> 1:1)	99	Ethyl-pentanal (12)	Oxo products (67)
		Methyl-hexanal (24)	
		Heptanal (31)	
		Cis/Trans 2-hexene (32)	
1-hexene (Toluene/water) (CO/ H <sub>2</sub> 3:1)	66	Total Oxo products (33)	Oxo products (33)
		Cis/ trans 2-hexene (33)	Isomerization (33)
1-hexene (cyclohexane/ Water) (CO/H <sub>2</sub> 1:1)	99	Ethyl-pentanal (19)	Oxo products (99)
		Methyl-hexanal (31)	
		Heptanal (48)	
Cyclohexene	79	Cyclohexylcarboxaldehyde (77)	Oxo products (77)
		Cyclohexane (2)	Hydrogenation (2)
2-methyl-2-pentene	2	2,2-dimethyl-pentanal (2)	Oxo products (2)
2,3-dimethyl-2-butene	17	2,2,3-trimethyl-butanal (17)	Oxo products(17)

\*Selectivity=  $(n_i / \sum n_i) \times 100$ ;  $n_i$  = mmols of product  $i$ ;  $\sum n_i$  = sum of all products measured as GC areas.

ruthenium carbonyl complex intermediate that becomes more soluble in the organic solvent, and migrates from the water layer. A similar behavior has been observed in other systems<sup>21</sup>. This effect precludes the possibility of reusing the catalyst in the biphasic systems tried. One of the possibilities is the production of a neutral carbonyl ruthenium complex more soluble in non-polar solvents; an IR of the yellowish organic layer solution, shows two terminal metal-carbonyl bands (2060 and 2029  $\text{cm}^{-1}$ ); the high frequency carbonyl values indicate that there is less metal-carbonyl back-donation and less metal-carbon strength, this is corroborated by the facility of complex decomposition when the organic solvent is evaporated, leaving a black metal residue, but is somewhat more stable in cyclohexane as solvent.

*1.2.- Cyclohexene - biphasic reaction:* Reaction conditions: Similar to reaction 1.1 B. Solvent (Toluene, 2 mL); substrate (cyclohexene, 2 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1

The reaction products are given in Table 2. The main product is the OXO compound cyclohexyl-carboxaldehyde and a small amount of hydrogenation product. The percent yield is somewhat smaller than for a linear olefin, as expected for a cyclic olefin.

*1.3.- 2-methyl-2-pentene - biphasic reaction:* Reaction conditions: Similar to reaction 1.1 B. Solvent (Toluene, 2 mL); substrate (2-methyl-2-pentene, 2 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1. The reaction products are given in Table 2. The reaction with this substituted olefin is very slow, giving a very low yield of OXO product.

*1.4.- 2-dimethyl-2-butene hydroformylation- biphasic reaction:* Reaction conditions: Similar to 1.1 B. Solvent

(Toluene, 2 mL); substrate (2,3 dimethyl-2-butene, 2 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1

The reaction products are given in Table 2. The OXO product is obtained in low yield, characteristic for a substituted olefin.

## 2. Hydroformylation of binary mixtures and synthetic naphtha:

In order to test the eventual behavior of a real naphtha and set the possible reaction conditions, the protocol starts trying out binary mixtures of representative olefins and then a standard mixture of four representative olefins called "synthetic naphtha" (see below).

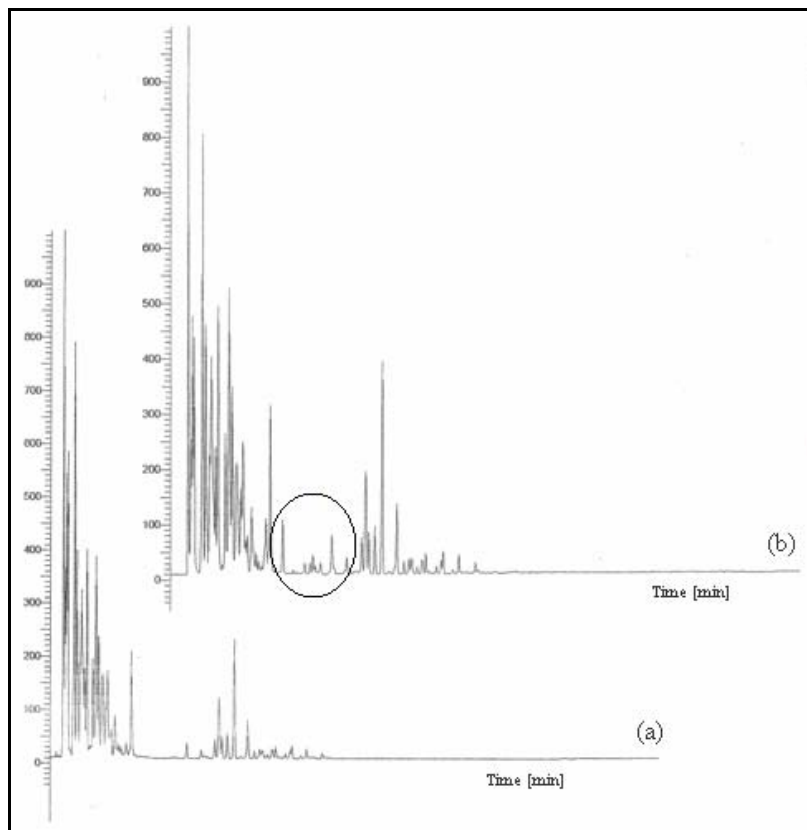
*2.1.- 1-hexene/cyclohexene - biphasic reaction:* Reaction conditions: Similar to 1.1 B. Solvent (Toluene, 2 mL); substrate (1-hexene, 1 mL; cyclohexene, 1 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1

The reaction products are shown in Table 3. Under this reaction conditions, the terminal olefin 1-hexene reacts completely, primarily to terminal aldehyde, while the cyclohexene gives the aldehyde product in 78 % yield. This ratio is to be expected since cyclic olefins react slower. It appears that the presence of cyclohexene inhibits the isomerization competing reaction for 1-hexene, since this is the fastest reaction with Ru complexes, and would be sensible to competition for the vacant sites with other complexing ligands as the cyclohexene olefin.

*2.2.- 2-methyl-2-pentene/2,3-dimethyl-2-butene - biphasic reaction:* Reaction conditions: Similar to 1.1 B. Solvent (Toluene, 2 mL); substrate (2-methyl-2-pentene, 1 mL; 2,3-dimethyl-2-butene, 1 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1. The reaction products are shown in Table 3. Under this reaction conditions, the substituted olefins give very low yields.

**Table 3.** Hydroformylation of binary mixtures and synthetic naphtha

Binary mixture	Conversión (%)	Products (%)	Selectivity (%)
<b>1-hexene/ cyclohexene</b>	1-hexene (100)	Aldehydes (100)	Oxo products
	Cyclohexene(78)	Aldehydes (78)	(100)
<b>2-methyl-2-pentene / 2,3-dimethyl-2-butene</b>	2	Aldehyde products	2
<b>Synthetic naphtha</b>	1-hexene (7)	Aldehydes (7)	Oxo products
	Cyclohexene (5)	Aldehydes (5)	(100)
	2-methyl-2-pentene (2)	Aldehydes (2)	
	2,3-dimethyl-2-butene(3)	Aldehydes (3)	



**Figure 1.** Gas chromatograph of real naphtha. Below: (a) before hydroformylation (b) after hydroformylation.

**2.3 Synthetic naphtha - biphasic reaction:** Reaction conditions: Similar to 1.1 B. Solvent (Toluene, 2 mL). Substrate: (Synthetic naphtha has the following volume composition: 1-hexene (32%); cyclohexene (11.4%); 2-methyl-2-pentene (28.3%); 2,3-dimethyl-2-butene (28.3%); total solution, 2 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1. The reaction products are given in Table 3. Under the reaction conditions, the total percent yield is low, giving mainly aldehyde products, with better yield for the unsubstituted olefins.

**2.4.- Real naphtha - Biphasic reaction:** Reaction conditions: Similar to 1.1 B. Solvent (Toluene, 2 mL); substrate (real naphtha, El Palito Refinery, Venezuela; 2 mL);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1; total time : 72 hr. The results are shown in Figure 1, corresponding to the chromatogram before and after the hydroformylation reaction; this figure clearly shows the region where the new oxygenated products appear (10 to 20 minutes retention times, circled in Figure 1, insert). The product distribution is complex, but the comparison permits the conclusion that new peaks appear in the region corresponding to medium sized

linear and substituted aldehydes and alcohols. The results obtained are encouraging, since the olefin percentage gets reduced (as demanded by the EPA regulations) and the percentage of oxygenated products increases, improving the fuel quality.

### 3. Mercury drop test:

In order to test the absence of metal particles in the biphasic mixtures, the 1-hexene hydroformylation reaction was tested adding a drop of liquid mercury to the reaction mixture. The results obtained are: a) Similar reaction conditions to 1.1 B. Solvent (Toluene, 2ml); substrate (1-hexene, 2ml);  $\text{RuCl}_2(\text{DMSO})_4$  (4 mg);  $\text{CO}/\text{H}_2$  1:1; no Hg: 99% total conversion; OXO products; b) Similar to a), but with 1 drop Hg: 80% total conversion; OXO products.

The results are similar, indicating that most likely no metal particles are responsible for the majority of the observed reaction for 1-hexene as substrate.

### Conclusions

The  $\text{RuCl}_2(\text{DMSO})_4$  complex is an active catalyst precursor for the hydroformylation reactions of 1-hexene both in homogeneous and biphasic organic solvent/water systems, favoring the linear aldehyde, but giving also

isomerization products. The hydroformylation reaction for cyclohexene is fairly good, giving also aldehyde products. For the substituted olefins 2-methyl-2-pentene and 2,3-dimethyl-2-butene, the percent yield is low. The hydroformylation reaction is also observed in binary mixtures of 1-hexene and cyclohexene, but is very low for the binary mixture of substituted olefins, as well as the reaction mixture known as synthetic naphtha. The preliminary results with a real naphtha show some hydroformylation activity in a slower reaction, showing some promise for fuel improvement. A test reaction with 1-hexene in the presence of liquid Hg, shows that no metallic Ru appears to be involved in this biphasic reactions.

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