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Artículo científico

Synthesis, characterization and Hydroformylation Catalytic Activity of 1-hexene of Water-soluble $RuCl_2(DMSO)_2(PySO_3Na)_2$ Complex

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Resumen

En el presente trabajo describimos la síntesis y caracterización del nuevo complejo acuosoluble $[Ru(Cl)_2(DMSO)_2(PySO_3Na)_2]$ donde $[PySO_3Na]$ es el ligando piridina p-sulfonato de sodio. Este complejo fue sintetizado por adición lenta del ligando a una solución metanólica del complejo cis-$[Ru(Cl)_2(DMSO)_4]$ bajo reflujo y atmósfera inerte. Este nuevo complejo fue caracterizado utilizando las técnicas de FT-IR y RMNH^1. El nuevo complejo mostró ser activo en la reacción catalitica de hidroformilación de 1-hexeno, sin embargo, no resultó ser muy activo en una prueba preliminar de hidroformilación catalítica con nafta real en medio bifásico. También se llevó a cabo la optimización de parámetros como tiempo, temperatura, presión y relación sustrato/catalizador usando 1-hexeno como sustrato. El sistema mostró pérdida de actividad durante las pruebas de reuso del catalizador, sin embargo mostró actividad en presencia de tiofeno y de mercurio metálico.

Palabras clave: hidroformilación, complejos de rutenio, nafta, catalizadores bifásicos.

Abstract

In this work we describe the synthesis and characterization of a new water soluble ruthenium complex $[Ru(Cl)_2(DMSO)_2(PySO_3Na)_2]$ (complex **1**); where $[PySO_3Na]$ is the sodium salt of p-sulphonated pyridine. Complex **1** was obtained by slow addition of ligand to a cis-$[Ru(Cl)_2(DMSO)_4]$ complex solution under inert atmosphere, the mixture was refluxed for 1 hour. Complex **1** was characterized by FT-IR and ^{1}H NMR techniques. Complex **1** was active in the catalytic 1-hexene hydroformylation and a preliminary test with real naphtha in a biphasic reaction mixture (water/toluene) shows little activity. Temperature, pressure, and substrate/catalyst ratio were studied with 1-hexene substrate. Catalysis with metallic particles was tested with a mercury drop trial giving negative results. The reuse of the aqueous phase in several reactions under the same experimental conditions showed loss of catalytic activity after the second reuse. Complex **1** is active for hydroformylation reaction of 1-hexene even in the presence of thiophene compounds.

Keywords: Hydroformylation, ruthenium complex, naphtha, biphasic catalyst.

Introduction

In the last years, there is a strong research effort toward synthesis and development of new ligands and complexes with structures and properties different from the traditional catalysts[1,2]. Rhodium complexes has been used mostly as catalyst in hydroformylation reactions, including real naphtha[3-7], and ruthenium complexes has been traditionally applied in hydrogenations reactions, but have also been tried with olefin hydroformylation[8-12], however there are few research reports using the metallic centers coordinated to amines ligands. These ligands are interesting because they show different electronic behavior maintaining the same steric effect. Pardey *et al*. reported hydrosterifications and hydroformylation-acetalyzation reactions with 1-hexene with soluble cationic rhodium carbonyl complexes with ligands such as pyridine, pycoline and lutidine supported on PVP[13,14]. Dutta *et al*. reported rhodium(I) dicarbonil complexes functionalized with aromatic amines giving excellent catalytic activity in the Monsanto process reaction[15]. In our research group, we reported the synthesis and catalytic activity of new complexes of Mo using p-sulphonated pyridine, p-cyanopyridine and sodium nicotinate ligands showing good results in 1-hexene hydroformylation reactions[16-19]. In this work, we report the synthesis, characterization and catalytic activity in hydroformylation reactions of 1-hexene and some preliminary trials with real naphtha of the novel $[Ru(Cl)_2(DMSO)_2(PySO_3Na)_2]$ complex.

Experimental

Materials and Methods

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Methanol solvent was previously dried by Grignard reaction and purified by distillation (purity; 99+%, NMR). The olefins, $RuCl_3.3H_2O$ (M.W. 262.07; 38.57% Ru) and the other reactants were reagent grade (Aldrich, purity 99+%). Toluene (Aldrich, purity, 99+%) and were used without further purification. Gases were purchased from AGA-Gases Venezuela. The synthesis of p-sulphonated pyridine of sodium was synthesized according to Suarez *et al.*[16]; the ruthenium complex was obtained from $RuCl_2(DMSO)_4$ (MW= 485.13g/mol) following the procedure of the literature[20] . The infrared spectra were recorded in a FT-IR Perkin Elmer 1600 using KBr. ^{1}H-NMR spectra were recorded on a Bruker 400MHz spectrometers using deuterated water as solvent. The analysis by gas chromatography was performed in a Perkin Elmer Chromatograph with flame ionization detector, the reaction products were analyzed using a methylsilicone Quadrex capillary column 50mx0.52µm. (initial oven temperature= 30°C, temperature ramp = 5°C/min, final temperature= 100°C). The products and reactants quantification was achieved by an integration method and the peaks were identified by comparison with pure samples analyzed under the same conditions in the chromatograph. The standards for 1-hexene, the isomerization, hydrogenation and hydroformylation products were run to compare the retention times. Catalytic runs were performed in a batch stainless steel autoclave reactor.

Catalytic Runs

In a general procedure (for changes in temperature, pressure, substrate/ catalyst relation, re-use, Hg drop test and thiophene test), in a Parr stainless steel reactor (10mL) with a special glass recipient with magnetic stirrer, the catalytic precursor (0.4 mg ,$5.79x10^{-4}$ mmol) was added in 5mL of water, and 1-hexene substrate in a 600/1 subs/cat ratio (1-hexene, 0.043mL ($3474x10^{-4}$mmol) in toluene (5mL total organic volume) (water and toluene were degassed with Ar and used without previous treatment). The solution was purged with CO gas three times and then charged at the required syngas pressure and heated to the desired temperature with stirring. The reaction temperature was varied from 25 to 125°C (298–398K) and the $CO:H_2$ (1:1) gas pressure was varied from 200 to 1000Psi (13.88 to 69.44atm). The reaction time was varied from 1 to 9 hours. For larger runs (run *vs.* time), where several samples would be taken, a Parr stainless steel autoclave (100mL) was used, with an internal glass liner, heating unit, temperature and stirring control, and a sample valve. Conditions for this trial were: toluene (30mL), water (30mL), substrate/catalyst ratio: 600:1 (1-hexene, 0.43mL, $3474x10^{-3}$mmol; catalyst: 4.0mg, near $5,79x10^{-3}$mmoles) Syngas pressure $CO:H_2$ (1000 Psi); Temperature: 100°C. The stirring rate was kept constant at 1600rpm to ensure thorough mixing and emulsion formation. Since the pH of the aqueous phase is important in biphasic systems[21-23], the aqueous phase was kept neutral in all the runs.

Synthesis of the $RuCl_2(DMSO)_2(PySO_3Na)_2$ complex

Using a round-bottom flask under Ar inert atmosphere, a solution with 0.103mmol $RuCl_2(DMSO)_4$ (MW. 485.13g/mol) and 10mL of dried methanol was prepared; the solution was stirred and refluxed for 10min. Another solution was prepared with 10 mL methanol and 0.206mmol of p- sulphonated pyridine of sodium ligand and this solution was slowly added with a syringe into the round-bottom flask. After addition, the solution was refluxed for 1 hour, allowed to cool and the volume reduced under vacuum, yielding an air-stable yellow solid (85% yield; MW.= 691.19g/mol)); decomposes > 220°C; it is soluble in polar solvents.

Results and Discussion

Synthesis and characterization

The new ruthenium complex $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ (complex **1**) was characterized by FT-IR and ^{1}H-NMR techniques. The FT-IR spectrum of complex **1** show the following characteristic bands: (ν_{CH})py, 3018cm^{-1} (medium, sharp); (ν_{CH})DMSO, 2927cm^{-1}(medium, sharp); ($\nu_{C\text{-}N}$), 1642cm^{-1} (medium, broad); ($\nu_{C\text{-}S}$),1386 cm^{-1} (strong, broad); (ν_{SO}), 1220cm^{-1} (strong, broad). The ^{1}H-NMR for complex **1** was recorded in deuterated water, (see Figure 1) shows two doublets of doublets between 7.78[H^a, doublet, 2H, J_{Hab}= 7.0]; and 8.62[H^b, doublet, 2H, J_{Hab}= 7.0]; corresponding to the protons from p- sulphonated pyridine ligand. Different signals from methyl protons are found in different magnetic environments because this complex could have DMSO ligands S or O bonded according to Alessio *et al.*[24]. In complex **1** we could find at least one DMSO ligand bonded through oxygen.

Time Effect

1-hexene hydroformylation with $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ complex: The new $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ complex has been tried in catalytic runs employing 1-hexene as a model olefin substrate. The oxygenated and isomerized reactions products are shown in Scheme 1. The reaction time was varied under conditions described in Table 1; at 6hr, the reaction has reached 50.5% yields of aldehyde compounds and 12.0% of isomerization reaction which appears as a competitive reaction, but eventually this product is converted into branched aldehydes.

Table 1: Time effect 1-hexene hydroformylation with [$RuCl_2(DMSO)_2(PySO_3Na)_2$]

Time (h)	**% Conversion Products**	**Isomerization**	**Hydroformylation**
0	0	0	0
1	5.8	2.5	3.3
1.5	5.1	1.8	3.3
2	5.7	0.8	4.9
2.5	14.6	6.7	7.9
5	27.6	8.1	19.5
6	62.5	12.0	50.5
7	94.2	14.9	79.3
9	99.9	9.1	90.8

Reaction conditions: Toluene: 30mL; water: 30mL; substrate/ catalyst ratio: 600:1 (1-hexene, 0.43mL/catalyst: 4.0mg, $5.79x10^{-3}$ mmoles); Syngas pressure: 1000Psi $CO:H_2$; T = 100°C)

After 9 hours of reaction time, most of the substrate has been consumed and the hydroformylation product is the main reaction product (90.8%) with some isomerization product still left (9.1%) after this reaction time. Under these hydroformylation conditions not significant hydrogenation products were detected in the GC analysis (less than 2% by relative peak areas). We propose that the relatively high CO pressure ($CO:H_2$ 1:1) (500psi) is enough to favor the hydroformylation addition to the double C=C bond. The isomerization reaction does not consume hydrogen or CO and usually requires softer reaction conditions. The reaction shows a TOF of 66 h^{-1}. (see Table 2).

Table 2: Activity of complex [$RuCl_2(DMSO)_2(PySO_3Na)_2$]

Complex	**Conversion (%)**	**TON**	Time (h)	TOF (h^{-1})
$RuCl_2(DMSO)_2(PySO_3Na)_2$	99.9	599	9	66

Temperature Effect

The effects of temperature are shown in Figure 2. The catalyst exhibit good results at temperatures above 100°C. This reaction at 75°C show low percent conversion to oxo products; when reaching 100°C major selectivity towards linear aldehyde is observed, with branched aldehydes in about 4/3 relation and oxygenated products formation with 90.8% conversion; at 125°C the system increases the selectivity to isomerization and decreases the hydroformylation product formation, but maintaining a branched to linear aldehyde relation of 3/4. This indicates that the isomerization reaction is competing favorably at 125°C, probably by decreasing the stability of the olefin π-complex required for CO/H_2 addition.

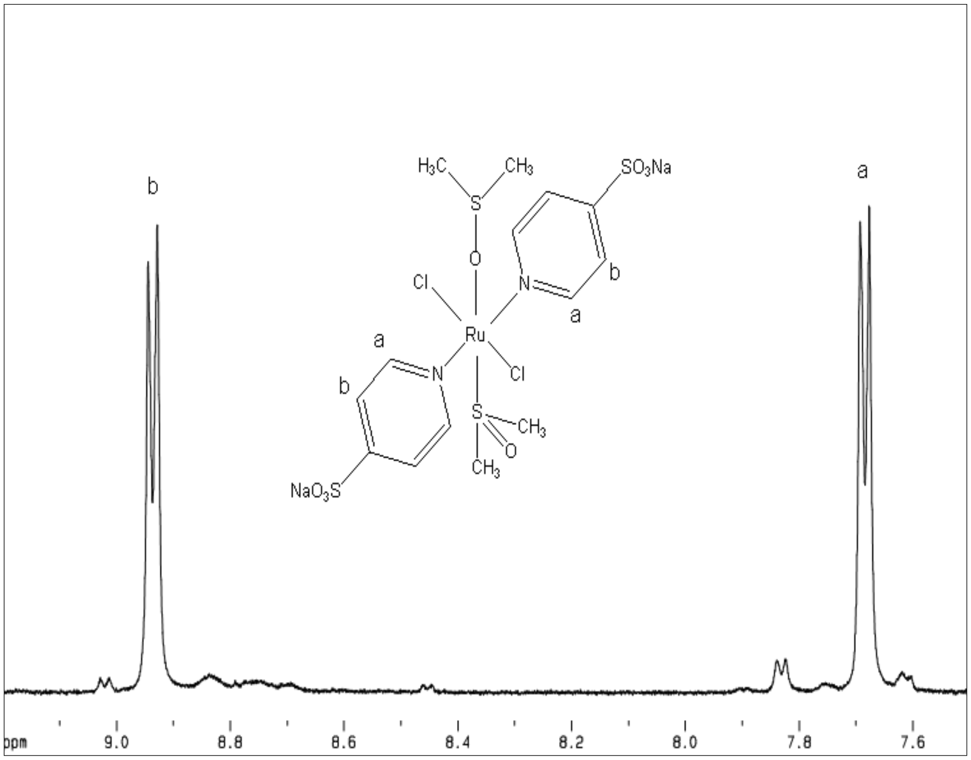
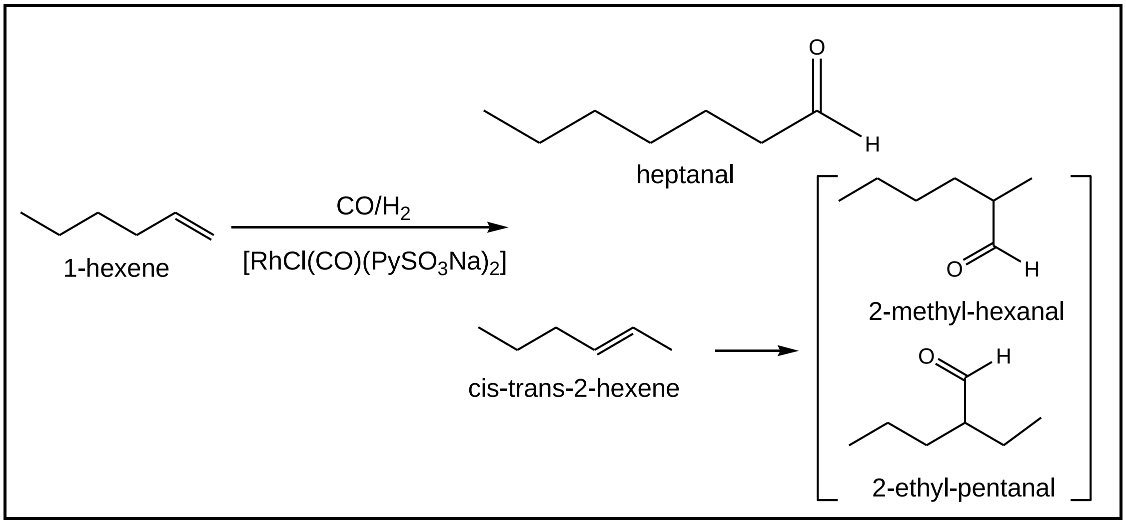


Fig. 1: ^{1}HNMR for complex (**1**), [$RuCl_2(DMSO)_2(PySO_3Na)_2$], in deuterated water.



Scheme 1: -hexene hydroformylation with catalyst [$RuCl_2(DMSO)_2(PySO_3Na)_2$] complex.

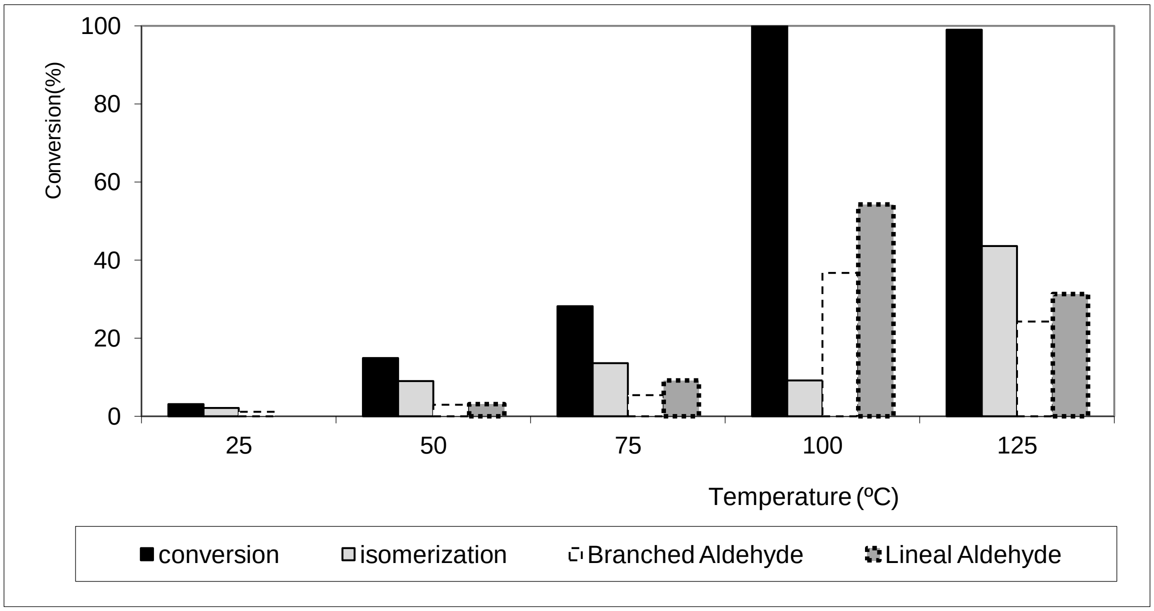


Fig. 2: Temperature effect. 1-hexene hydroformylation with complex [$RuCl_2(DMSO)_2(PySO_3Na)_2$]. Reaction conditions: syngas pressure: 1000Psi ($CO:H_2$), substrate/catalyst ratio: 600:1(1-hexene 0.043mL/ catalyst: 0.4mg, $5.79x10^{-4}$mmoles), reaction time 9h.

Pressure Effect

The results varying syngas pressure in 1-hexene hydroformylation reaction are shown in Figure 3. At lower pressures the isomerized product is favored, reaching 67.5% and 31.2% conversion of total oxo products (400psi); at moderate pressures the conversion towards oxygenated products increases notably and isomerization products decrease rapidly; at syngas pressure of 1000psi gives good selectivity to linear aldehyde, with branched aldehyde in a 3/4 realtion, but this fact is not so important for our application with real naphtha, where it is enough to obtain oxygenated products. Al 1000psi total pressure, the 500psi of CO partial pressure, is sufficient to surpass the isomerization competing reaction, but remembering that the internal-hexene isomers are needed to produce the branched aldehydes. The product distribution is the result after 9 hour reaction time.

Ratio Substrate/ Catalysts

Table 3 shows the effect of substrate /catalyst ratio at a fixed total reaction time (9hr). The activity increases with a greater catalyst proportion with greater conversion towards oxygenated products favoring linear aldehydes. When the relation corresponds to a lower relative amount of catalyst, the percent conversion drops considerably (for example at 4000/1, the conversion to oxygenated products (aldehydes) has reduced to 35.8 % , and the isomerization competing reaction remains at 23.1%)

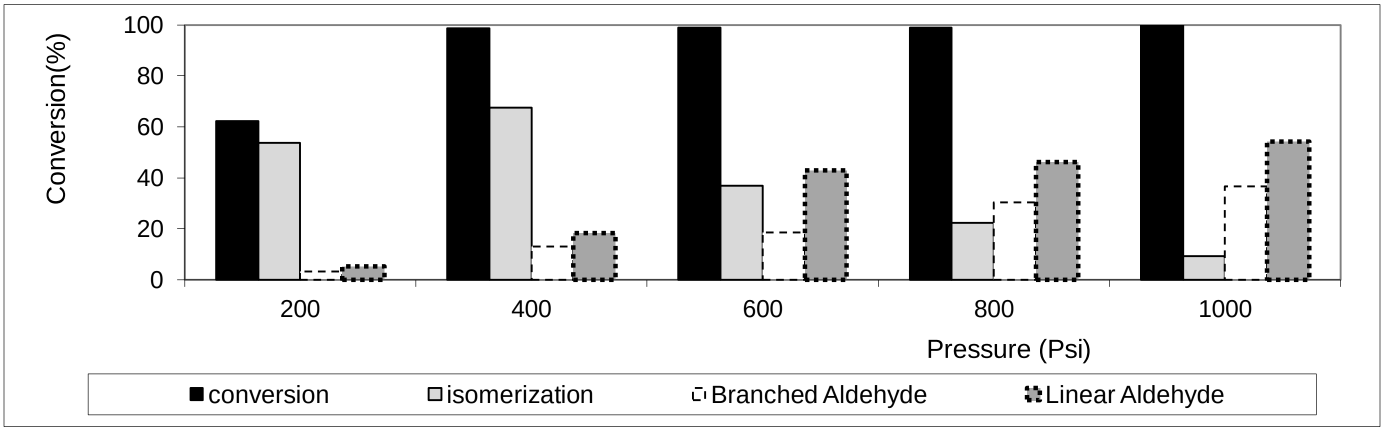


Fig. 3: Syngas pressure effect: 1-hexene hydroformylation with complex $[RuCl_2(DMSO)_2(PySO_3Na)_2]$. Reaction conditions: Temperature 100°C, substrate /catalyst ratio: 600:1(1-hexene 0.043mL/ catalyst: 0.4mg, $5.79x10^{-4}$mmoles) , reaction time 9h.

Table 3: Substrate\catalyst ratio effect. 1-hexene hydroformylation with $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ complex.

Sust/Cat Relationship	(%) Conversion	(%) Isomerization	Branched Aldehyde	Linear Aldehyde	Total Oxigenated
600/1	99.9	9.1	36.7	54.1	90.8
1000/1	99.5	25.6	44.2	29.7	73.9
2000/1	93.5	1.7	51.9	39.9	91.8
3000/1	81.7	20.9	36.3	24.2	60.8
4000/1	58.9	23.1	12.7	23.1	35.8

Reaction conditions: Syngas pressure; 1000psi, Temperature 100°C, reaction time 9h. substrate/catalyst: variable relation)

Catalyst Reuse

One important aspect in this type of biphasic catalytic system is the possibility of reusing the catalyst without losing activity. Once completed the run, the aqueous phase that contains the water soluble catalyst was reused. This process was repeated two times. The results are presented in Table 4. The reaction showed appreciable loss of catalytic activity. At the end of each reaction, a yellowish organic layer was observed; presumably some catalyst was being transferred to the organic layer, perhaps as a stable carbonyl intermediary. Therefore a test run was tried with a higher quantity of catalytic precursor without the presence of substrate under the same reaction conditions; after that the organic layer was separated and the solvent was removed under reduced pressure until dry; this solid was analyzed by FT-IR and two characteristic carbonyls stretching at 1999cm^{-1} and 2059cm^{-1} were found. This behavior was observed also with the catalytic precursor $RuCl_2(DMSO)_4$[25], under hydroformylation conditions. In hydrogenation reactions of 1-hexene, under hydrogenation conditions, this does not happen[8].

Table 4: Catalyst reuse. 1-hexene hydroformylation with $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ complex

Reuse	% Conversion	% Isomerization	Branched Aldehyde	Linear Aldehyde
0	99.9	9.1	36.7	54.1
1	37.33	17.3	6.5	13.5
2	15.6	10.3	2.3	3

Mercury drop Assay

The mercury drop assay[26] was performed to confirm that the hydroformylation reaction proceeds in a homogeneous phase, and not through suspended metal particles coming from catalyst decomposition, which could be intervening in the hydroformylation reaction. Table 5 shows the result of reactions products with and without a mercury drop showing that there is no appreciable change in the total conversion of products.

Table 5. Mercury drop essay: 1-hexene hydroformylation with $[RuCl_2(DMSO)_2(PySO_3Na)_2]$ complex

Hg	% Conversion	% Isomerization	Branched Aldehyde	Linear Aldehyde
No	99.9	9.1	36.7	54.1
Yes	95.3	3.7	48.7	42.9

Thiophene Assay

Due to great quantities of sulphurated products in Venezuelan naphthas, it was necessary to test the effect of thiofene addition to the catalytic system and verify if this is sensible or not to the presence of sulphurated compounds. The results are shown in Table 6 where we can appreciate that the addition of different quantities of thiophene show no appreciable effect in the catalytic system, indicating low sensitivity of the catalyst to this sulphurated compound. A similar result has been observed with an analogous Rh complex under hydroformylation conditions[7,27].

Real naphtha Catalysis

The principal goal in this work is the application of ruthenium biphasic system for obtaining fuels with high proportion of oxygenated products which contribute to better the quality and performance of gasoline through a simple and unique process.

Table 6: Thiophene assay: 1-hexene hydroformylation with [$RuCl_2(DMSO)_2(PySO_3Na)_2$] complex

Thiophene	% Conversion	% Isomerization	Branched Aldehyde	Linear Aldehyde
50 ppm	98.2	10.8	35.0	52.4
150 ppm	99.2	9.7	35.9	53.4
0 ppm	99.9	9.1	36.7	54.1

We used real light naphtha from FCC El Palito Refinery-Venezuela, with high contents of olefinic compounds[28]. The GC chromatograms obtained from the liquid phase before and after catalytic reaction are shown in Figure 4. Between 10 and 20min retention time, we observe the presence of a few reaction products of hydroformylation of olefins. So, this catalyst shows only slight hydroformylation reactions of real naphtha. Compared with the Rh system[7], which shows a very strong tendency to hydroformylate the same real naphtha, with good production of aldehydes (that appear in the 10 to 20min retention time range), the Ru system would require stronger reaction conditions, including longer reaction times.

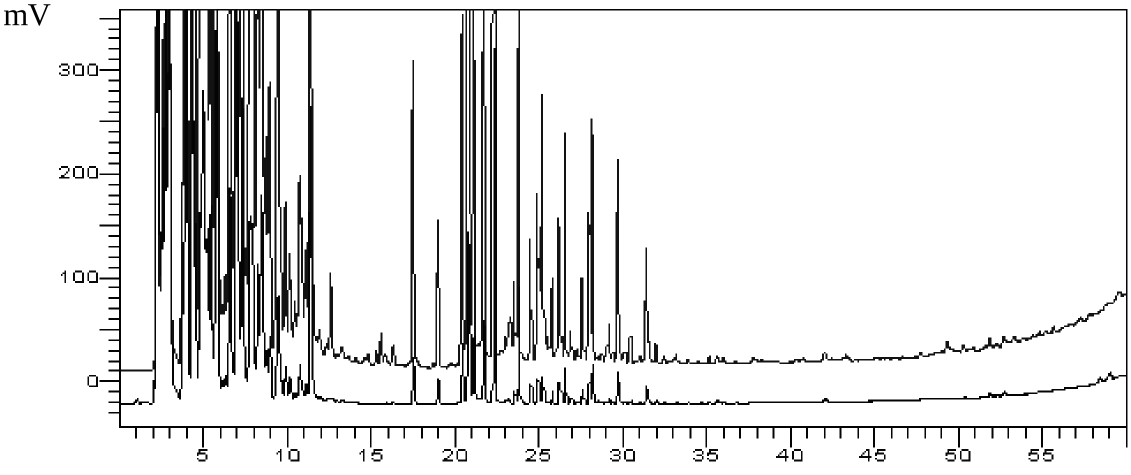


Fig. 4: Real naphtha hydroformylation with $RuCl_2(DMSO)_2$ $(PySO_3Na)_2$ complex. Catalytic Precursor: 10mg, naphtha: 5mL, aqueous phase: 5mL. Pressure (CO/H_2) (1:1) 1000psi, Temperature: 100ºC, Time: 24h, Ratio subs/cat: near 600:1).

Conclusion

A new water soluble complex of ruthenium [$RuCl_2(DMSO)_2(PySO_3Na)_2$] was synthesized and characterized. This complex showed good activity in biphasic hydroformylation of 1-hexene. The mercury drops assay shows no affect in the hydroformylation reaction, in this case the reaction is probably occurring without the presence of metallic particles. The presence of thiophene in the reaction medium does not diminish the catalyst activity, showing low catalyst sensitivity to this sulphurated compound. This system was not recycled successfully due to leaching to the organic phase and show low activity in the hydroformylation reaction of real naphtha under the reaction conditions tried.

Acknowledegments

To Professor Bernardo Fontal in occasion for his 70th birthday.

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