

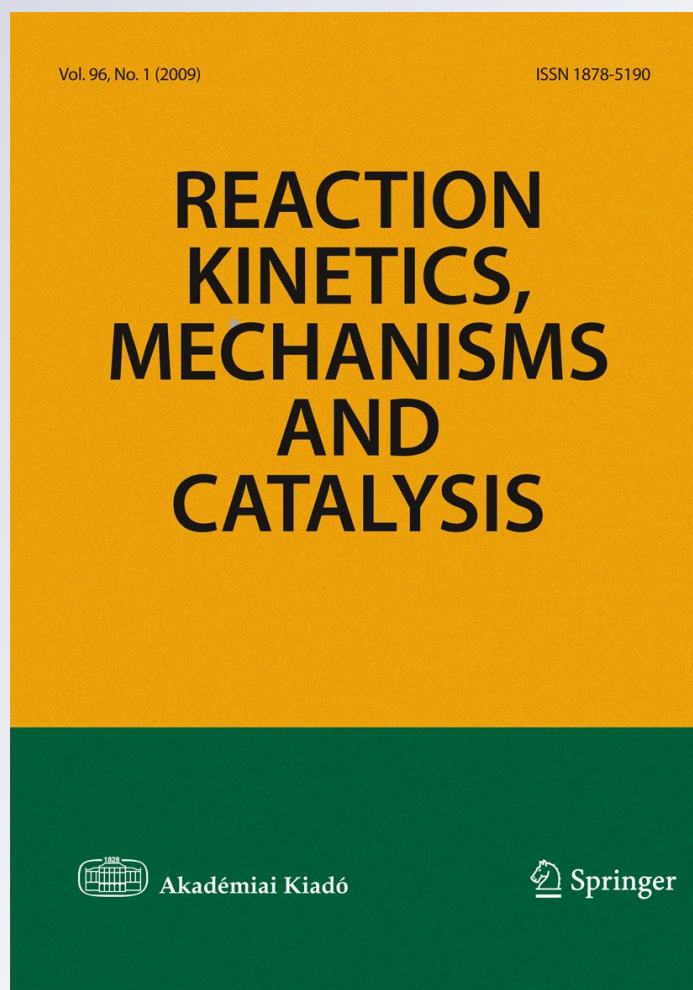
Synthesis, characterization and hydroformylation catalytic activity of a water-soluble $RhCl(CO)(PySO_3Na)_2$ complex using 1-hexene and real naphtha

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Synthesis, characterization and hydroformylation catalytic activity of a water-soluble $\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2$ complex using 1-hexene and real naphtha

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Abstract In this work, we describe the synthesis and characterization of a new water soluble $[\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2]$, complex (**1**); where $[\text{PySO}_3\text{Na}]$ is the sodium salt of *p*-sulfonated pyridine ligand. Complex (**1**) was obtained in methanol, reacting the dried sodium salt of *p*-sulfonated pyridine ligand with $[\text{Rh}(\text{Cl})(\text{CO})_2]_2$ complex under inert atmosphere. Complex (**1**) was characterized by FT-IR and ^1H NMR techniques. Complex (**1**) was active in the catalytic hydroformylation of 1-hexene and real naphtha in a biphasic (water/toluene) system. The effects of reaction time, temperature and syngas pressure were studied with 1-hexene as a substrate. Formation of metallic particles was tested with a mercury drop trial, giving negative results. Reuse of the aqueous phase for several times under the same conditions showed little catalytic activity loss. Complex (**1**) was active for the hydroformylation reaction of 1-hexene, in the presence of thiophene compounds, showing better performance in comparison with water soluble rhodium analogues.

Keywords Hydroformylation · Rhodium complex · Naphtha · Biphasic catalyst

Introduction

Ecological reasons make technological process development necessary to obtain clean or ecological fuels [1–3]. High contents of olefins in fuel produces severe damage to engines as a consequence of polymerization reactions. Furthermore, it is necessary to decrease the olefin quantities due to standard regulations [4]. Traditionally, rhodium complexes have been used as catalysts in hydroformylation reactions, mostly using ligands as phosphines, phosphites or phosphinites [5, 6]. However, there are few reports

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describing rhodium complexes with amine ligands in biphasic hydroformylation reactions which can be compared and show good performance in their catalytic activity as traditional rhodium with sulfonated phosphines or analogue complexes [7–11]. At present, our research is directed toward the synthesis of the sodium salt of sulfonated pyridine [12, 13] as a water-soluble ligand with different metallic centers. The principal goal in this work is the application of rhodium biphasic systems to obtain fuels with high oxygenated products proportion, which would contribute to the improvement of the quality and performance of gasoline through a simple and unique process and finding a friendly environment alternative to avoid the use of ethanol as fuel additive [14–19].

Experimental

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Methanol was previously dried by the Grignard reaction and purified by distillation. The olefins, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and the other reactants were reagent grade (Aldrich). Toluene (Aldrich) was used without further purification. Gases were purchased from AGA-Gases Venezuela. The synthesis of the sodium salt of *p*-sulfonated pyridine was synthesized according to Suarez et al. [16]; the rhodium dimer complex was obtained from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and CO using the modified method described by Reyes et al. [17].

Physical measurements

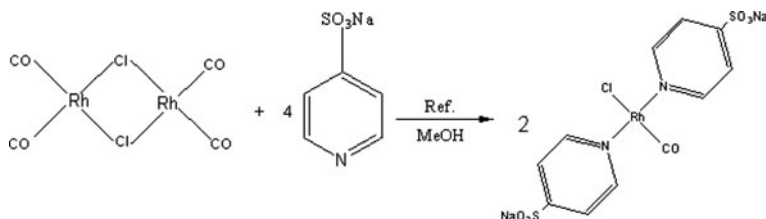
The infrared spectra were recorded in a FT-IR Perkin Elmer 1600 using KBr. ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer using deuterated water as solvent. The analysis by gas chromatography was done in a Perkin Elmer chromatograph with flame ionization detector; the reaction products were analyzed using a methyl silicone Quadrex capillary column 50 m \times 0.52 μm . The product and reactant 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.

Synthesis of $\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2$

The synthesis of complex (1) is shown in Scheme 1; using a round-bottom flask under inert Ar atmosphere. To a dry methanol (10 mL) solution with 0.257 mmol rhodium dimer complex, a methanolic solution (10 mL) with 1.028 mmol of sodium salt of *p*-sulfonated pyridine ligand was slowly added with a syringe and then heated to reflux for 4 h. This solution was allowed to cool and the solvent was removed under reduced pressure, giving an orange solid (80% yields); 190–195 °C melting point and it is soluble in polar solvents, even water.

Catalytic runs

In a general procedure, runs were carried out in a Parr steel autoclave (10 or 100 mL with a sampling valve, for variable optimization), with special glassware and



Scheme 1 Synthesis of $\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2$, complex (1)

magnetic or mechanical stirring. The solution was purged with CO gas three times and then charged at the required syngas pressure and heated to the desired temperature with strong stirring to ensure thorough mixing and emulsion formation. The reaction temperature was varied from 25 to 125 °C (298–398 K); $\text{CO}:\text{H}_2$ (1:1) syngas pressure was varied from 200 to 1,000 psi (13.88–69.44 atm). The reaction time was optimized from 1 to 4 h. Conditions for reaction: toluene (5 or 30 mL), water (5 or 30 mL), 0.0045 mol of substrate 1-hexene, 7.5×10^{-3} mmol of catalyst precursor, substrate/catalyst ratio: 600:1; syngas pressure ($\text{CO}:\text{H}_2 = 1$), 1,000 psi.

Results and discussion

Characterization

The new rhodium complex (1), $[\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2]$ was characterized by FT-IR and ^1H NMR techniques. The FT-IR spectrum of the complex (1) shows the following characteristic bands: (ν_{CH}) $3,100\text{ cm}^{-1}$ (weak, sharp); (ν_{CN}) $1,600\text{ cm}^{-1}$ (medium, broad); (ν_{CS}) $1,415\text{ cm}^{-1}$ (medium, sharp); (ν_{SO}) $1,215\text{ cm}^{-1}$ (strong, broad); (ν_{CO}) $2,016\text{ cm}^{-1}$ (medium, broad) (CO stretching band characteristic of coordinated carbonyl ligand); (ν_{OH}) $3,464\text{ cm}^{-1}$ (strong, broad) (corresponding to the hydration sphere of the sulfonate group) [16]. The ^1H NMR for complex (1), in deuterated water shows two doublets of doublets between 7.77 [H^{a} , doublet, 2H, $J_{\text{Hab}} = 5.6\text{ Hz}$]; and 8.62 [H^{b} , doublet, 2H, $J_{\text{Hab}} = 5.2\text{ Hz}$]; corresponding to the protons from the sodium salt of *p*-sulfonated pyridine ligand (Fig. 1).

1-Hexene hydroformylation reaction with $[\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2]$ complex

Time effect

The new complex (1), $[\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2]$, was tried in a catalytic run employing 1-hexene as a model olefin substrate. The oxygenated and isomerized reactions products are shown in Scheme 2. The reaction time was optimized under conditions described in Table 1. At 210 min, the reaction is almost complete, and had reached 49.9% yields of linear aldehyde and 45.6% of branched aldehyde with selectivity towards 2-methyl-hexanal product. The total conversion towards products is 99.8%.

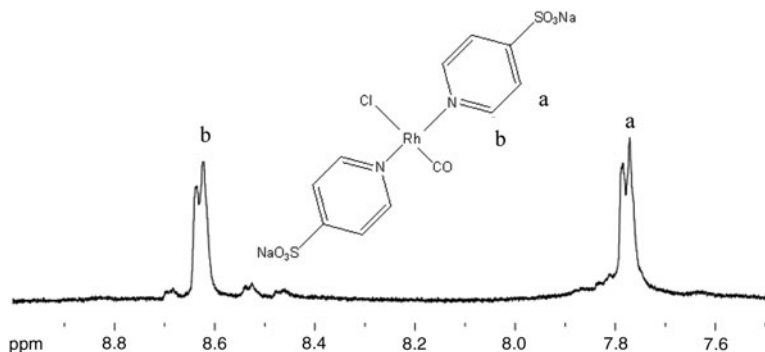
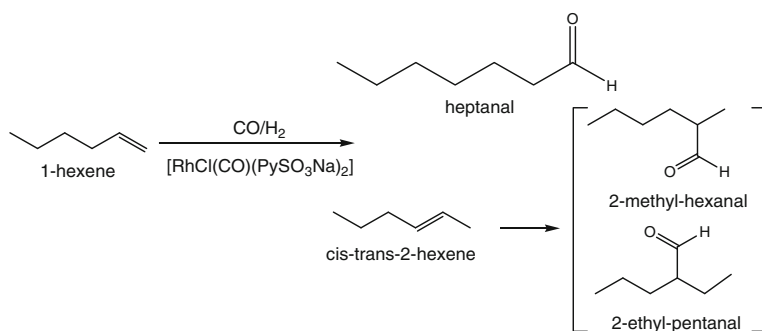


Fig. 1 ^1H NMR for complex (**1**), $[\text{RhCl}(\text{CO})(\text{PySO}_3\text{Na})_2]$, in deuterated water



Scheme 2 1-hexene hydroformylation with catalyst complex (**1**)

Table 1 Time effect: 1-hexene hydroformylation with complex (**1**)

Selectivity (%)						
Time (min)	%Conversion products	Cis-2-hexene	Trans-2-hexene	2-Methylhexanal	2-Ethylpentanal	Heptanal
0.5	5.6	1.0	0.2	–	–	4.4
1.0	11.3	1.2	0.8	1.6	–	7.7
1.5	18.9	6.9	2.0	1.1	4.0	4.9
2.0	34.3	7.4	3.4	8.9	1.1	13.5
2.5	81.5	7.4	2.3	29.1	1.0	41.7
3.0	98.4	6.4	1.5	40.1	1.0	49.4
3.5	99.8	2.6	0.5	45.6	1.2	49.9

Toluene: 30 mL; water: 30 mL, catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; syngas pressure: 1,000 psi ($\text{CO}:\text{H}_2 = 1$); temperature: 100 °C

The isomerization reaction appears like a competitive reaction, but, eventually this product is converted into branched aldehydes. The optimal time to this reaction was 3.5 h. The reaction shows a TON of 599 and TOF of 171 h^{-1} .

Temperature effect

The effects of reaction temperature are shown in Fig. 2. The catalyst exhibits good results (reactions conditions: syngas pressure: 1,000 psi ($\text{CO}:\text{H}_2$), substrate /catalyst ratio 600:1). At 75 °C, the reaction shows good conversion to oxo products; when reaching 100 °C, there is major selectivity to the linear aldehyde and oxygenated products formation. At higher temperatures (125 °C), the percent conversion decreases (91.4%) and more branched aldehydes are produced, with a notable isomerization increase, which could explain the higher branched aldehyde production.

Syngas pressure effect

The effects of changes in syngas pressure are shown in Fig. 3. Lower pressures favor the isomerized product, (81.6%) and lower (15.0%) oxo products conversion.

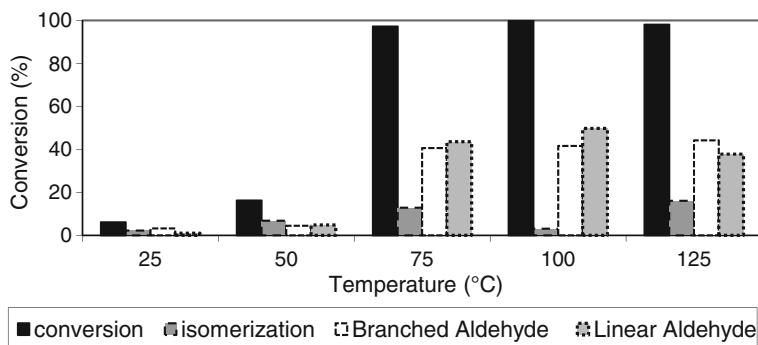


Fig. 2 Temperature effect in 1-hexene hydroformylation with complex (1). Toluene: 5 mL; water: 5 mL; catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; syngas pressure: 1,000 psi ($\text{CO}:\text{H}_2 = 1$); time: 3.5 h

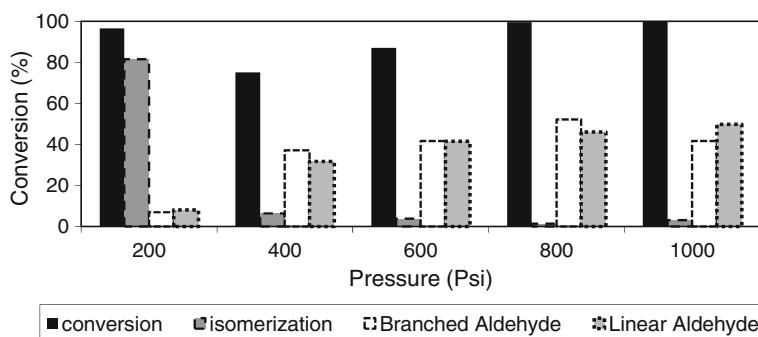


Fig. 3 Syngas pressure effect in 1-hexene hydroformylation with complex (1). Toluene: 5 mL; water: 5 mL; catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; $\text{CO}:\text{H}_2 = 1$; time: 3.5 h

At moderate pressures, the oxygenated product conversion increases and the conversion of isomerization products decreases rapidly, with a slight increase to linear aldehyde at 800 psi. At 1,000 psi oxygenated products are still produced in good yield.

Catalyst reuse

An important aspect of biphasic catalysis is to explore the catalytic efficiency of recycling the catalytic system. Once the run completed, the organic phase was removed with a syringe and the aqueous phase reused, after adding fresh reactants. This process was repeated five times, and the results are presented in Table 2. Little appreciable catalytic activity loss is observed; this experiment clearly shows the recycling capabilities of this catalytic system for the hydroformylation of olefins.

Mercury drop assay

The mercury drop assay was performed to confirm that the hydroformylation reaction proceeds in a homogeneous phase and not through metal particles from complex decomposition. The results are presented in Table 3; the reaction does not change appreciably in the presence of the mercury drop compared with the reaction in the absence of Hg.

Thiophene assay

Venezuelan naphthas contain high concentration of sulfurated compounds, thus it is important to test the catalytic system to the possible effects of model sulfurated

Table 2 Catalyst reuse: 1-hexene hydroformylation with complex (1)

Reuse	Total conversion (%)
0	99.7
1	99.9
2	93.3
3	97.9
4	95.3
5	99.9

Toluene: 5 mL; water: 5 mL, catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; syngas pressure: 1,000 psi (CO:H₂ = 1); time: 3.5 h

Table 3 Mercury drop assay: 1-hexene hydroformylation with complex (1)

Hg drop	Conversion (%)	Isomerization (%)	Branched aldehyde (%)	Linear aldehyde (%)
0	99.8	8.1	41.8	49.9
1	98.9	1.4	45.7	51.8

Toluene: 5 mL; water: 5 mL, catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; syngas pressure: 1,000 psi (CO:H₂ = 1); time: 3.5 h

Table 4 Thiophene assay: 1-hexene hydroformylation with complex (1)

Thiophene (ppm)	Conversion (%)	Isomerization (%)	Branched aldehyde (%)	Linear aldehyde (%)
0	99.8	8.3	41.6	49.9
50	98.7	0.5	53.4	44.8
150	98.2	1.0	53.0	45.2

Toluene: 5 mL; water: 5 mL, catalyst: 0.004 mg (7.5×10^{-3} mmol); 1-hexene: 0.373 mg (4.5×10^{-3} mol); substrate/catalyst ratio: 600:1; syngas pressure: 1,000 psi ($\text{CO}:\text{H}_2 = 1$); time: 3.5 h

compounds such as thiophene. The results of adding different thiophene concentrations are shown in Table 4. Additions of up to 150 ppm of thiophene, show no appreciable changes in the reaction products, indicating low catalyst sensitivity to this compound.

Real naphtha catalysis

Real light naphtha from FCC El Palito Refinery, Venezuela, with the following composition: olefins: 43.50%; aromatics: 3.50%; naphthenic: 13.00%; paraffinic: 40.00%; was treated with the catalytic system. Different oxygenated products as aldehydes and ketones were run as standard to know the retention times and compare with naphtha chromatograms. The GC chromatograms obtained from the liquid phase before and after the catalytic reaction are shown in Fig. 4 (24 h) and Fig. 5 (48 h) (overlap GC, before and after catalytic runs, reaction conditions are given for each reaction). Between 10 and 20 min retention times, the reaction products of olefins hydroformylation are observed. For 48 h of reaction time, the quantity of hydroformylated or oxygenated products increases in comparison with the 24 h reaction. [18–20].

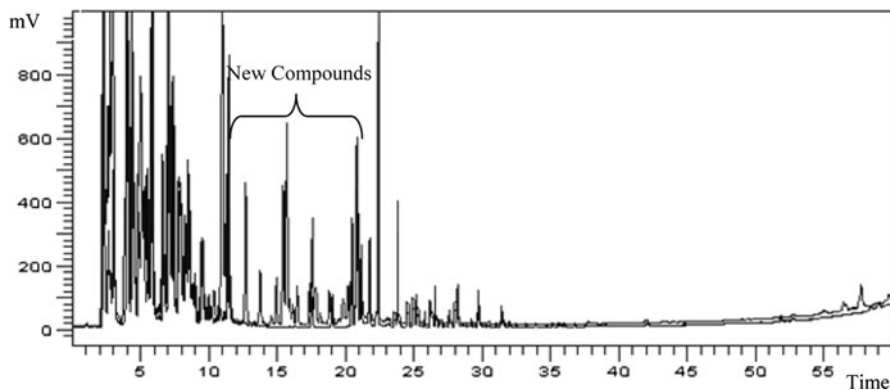


Fig. 4 Real naphtha hydroformylation with complex (1). Toluene: 5 mL; water: 5 mL, catalyst: 10 mg (0.0189 mmol); naphtha: 5 mL, aqueous phase: 5 mL. Syngas pressure, 1,000 psi ($\text{CO}:\text{H}_2 = 1$) temperature: 100 °C, time: 24 h

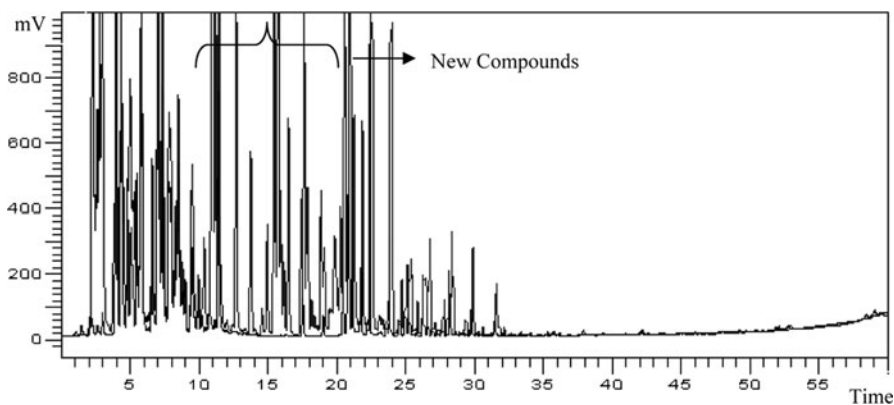


Fig. 5 Real naphtha hydroformylation with complex (1). Toluene: 5 mL; water: 5 mL, catalyst: 10 mg (0.0189 mmol); naphtha: 5 mL, aqueous phase: 5 mL. Syngas pressure, 1,000 psi (CO:H₂ = 1), Temperature: 100 °C, Time: 48 h

Conclusions

A new water-soluble complex of rhodium [RhCl(CO)(PySO₃Na)₂], was synthesized and characterized. This complex shows good catalytic activity in biphasic hydroformylation of 1-hexene, favoring the linear aldehyde. The different reaction parameters were optimized. The mercury drop assay has no effect on the hydroformylation reaction, indicating a homogeneous reaction. The presence of thiophene in the reaction medium does not reduce the catalytic activity. This system was recycled five times without important catalytic activity loss. The system shows good activity in the hydroformylation reaction of real light naphtha.

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