

Synthesis, characterization and catalytic activity in the hydroformylation of 1-hexene and styrene of water-soluble rhodium complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ (Part 1)

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Abstract

The synthesis and full characterization of the water-soluble complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ (**I**), where TPPMS is $(\text{C}_6\text{H}_5)_2\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$ and Pz pyrazolate, is described. Complex **I** was obtained by ligand exchange procedures under inert atmosphere and characterized by FT-IR, ¹H NMR, ¹H{³¹P} NMR, ³¹P NMR and FAB-MS techniques. These analyses confirmed that there are two pyrazolate bridging ligands in an exobidentate orientation, giving a C_{2v} symmetry to the complex. The molecular weight of **I** was confirmed by FAB-MS, indicating the molecular formula stated above. The complex was active in the catalytic hydroformylation of 1-hexene and styrene in a two-phase reaction medium. Heptanal was the main product obtained for 1-hexene, while 2-phenylpropanal and 3-phenylpropanal were obtained from styrene. At the end of the reaction, all the metal remained in the aqueous phase, indicating that no metallic leaching observed during the catalytic reaction.

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1. Introduction

Catalyst recovery and recycling is a great concern for chemical processes in homogeneous catalysis. For this reason, biphasic catalysis has been the center of attention for the last years, fundamentally based in the possibility of an easy recovery of the catalyst for simple decantation. The interest in water-soluble organometallic complex swiftly has increased since the development of the Rhône-Poulenc/Rührchemie biphasic catalysis process for the hydroformylation of propene to *n*-butyraldehyde. The development of water-soluble catalyst for the hydrogenation and hydroformylation of olefins has attracted a great deal of publications [1,2]. Mainly, mononuclear complexes based on rhodium and different kind of ligands majority phosphine and phosphite has been used for olefin hydroformylation [3]. However, the use of binuclear rhodium

complexes bearing bridge ligands as catalyst precursor in the hydroformylation of olefin has been paid less attention. For example, Kalck et al. [4] reported high catalytic activity in the hydroformylation of 1-hexene with the complex $[\text{Rh}(\mu\text{-S-Bu})(\text{CO})(\text{P}(\text{OMe})_3)]_2$ (**1**) at low pressure in a homogeneous system. Kalck [5] also reported the synthesis of *cis*- $\text{Rh}_2(\mu\text{-}t\text{-Bu})(\mu\text{-Pz})(\text{CO})_2\text{L}_2$, (**2**), where L is trimethylphosphite, triphenylphosphite or triphenylphosphine, which showed a lower catalytic activity in comparison with the complex (**1**). An elegant work in bimetallic hydroformylation was described by Stanley and co-workers during the synthesis and characterization of the complex $(\text{Rh}_2(\text{NBD})_2\text{P-P})$ with P-P different bidentate phosphine [6]. They proposed the first mechanism for bimetallic hydroformylation where they prove a cooperative effect of both metal [7]. Moreover, Usón et al. [8a] reported the catalytic activity of the binuclear rhodium complex with pyrazolate bridge ligands in the hydroformylation reaction of 1-heptene. The complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{PPh}_3)]_2$ showed a moderate catalytic activity and increases the selectivity to octanal from 40 to 60%, and no hydrogenation

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products were obtained during the reaction. In this work, the synthesis, characterization and catalytic activity of the water-soluble complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ (**I**) is reported, where TPPMS is $(\text{C}_6\text{H}_5)_2\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$ and Pz pyrazolate in the hydroformylation reaction of 1-hexene and styrene in a two phases medium.

2. Experimental

2.1. General procedure

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques [9]. All the organic solvents were dried and purified by distillation and were stored under inert atmosphere. The olefins and their respective saturated products were reagent grade (Aldrich). Water was deionized and treated with nitrogen prior to use. TPPMS was prepared according to the modified reported procedures [10,11]. Rhodium trichloride and pyrazolic acid (Aldrich) were used without further purification. Gases were purchased from AGA-Gases, Venezuela. The complex (**I**) was prepared according to a previous report [12]. The infrared spectra were recorded in a Perkin-Elmer Spectrum 1000 FT-IR using samples as KBr disks. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker 500 MHz spectrometers, using deuterated solvents. All chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (^1H) or 85% H_3PO_4 (^{31}P). GC analyses were performed on a Hewlett-Packard 5890 Series II chromatograph with a flame ionization detector coupled to a HP integrator 3392-A and HP-1 methylsilicone, 30 m \times 0.53 mm column. Quantification was achieved by using the internal standard (naphthalene) method and the peaks were identified by comparison with pure samples analyzed by a GC 5890-MS 5971 coupled system using Quadrex PONA 5% phenylmethyl silicone. The UV-Vis spectra were taken in a diode array H/P 8452 spectrometer. Mass spectra were obtained in a Kratos ZAB BEQQ spectrometer with E1 and FAB (glycerol matrix) 12 eV. Atomic absorption analyses were performed with a Perkin-Elmer 5000 instrument.

2.2. Catalytic runs

In a typical experiment, an aqueous solution of the rhodium catalyst (20 ml, 1.5×10^{-3} M) and a heptane solution of the substrate (18 ml, 1.66×10^{-3} mol) were introduced into a glass-lined stainless steel autoclave (Parr, 160 ml). The solution was purged with syngas mixture (three times) and then charged at the required syngas pressure and heated to the desired temperature with stirring. The reaction temperature was varied from 60 to 140 °C (313–413 K); $\text{CO}:\text{H}_2$ 1:1 gas pressure varied from 50 to 120 psi (3.40 to 81.6 atm) and the substrate/catalyst ratio varied from 25:1 to 600:1 and the stirring rate was keeping constant at 630 rpm.

The liquid samples were removed from the reactor vessel and analyzed by GC and GC-MS techniques.

3. Results and discussion

3.1. Synthesis and characterization

The new rhodium complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ (**I**) was prepared according to a method reported previously by our group [12]. A complete characterization of complex (**I**) was based from the spectroscopy data obtained using FT-IR, ^1H NMR, $^1\text{H}\{^{31}\text{P}\}$ NMR, ^{31}P NMR and FAB-MS.

The FT-IR spectrum (nujol mull) of the complex (**I**) shows a strong sharp CO stretching band (ν_{CO}) at 1975 cm^{-1} characteristics of two carbonyl ligands coordinated in a similar chemical environment, in which each Rh center has one CO ligand [13]. It is worthy to mention that if the CO ligands were coordinated in *cis*-position, we could observe two stretching signals [13].

Furthermore, the ^1H NMR (CD_3OD) for complex (**I**) shows a series of signals corresponding to the TPPMS hydrogen between 7.2 and 8.0 ppm. The pyrazolyl hydrogen are located at 6.4 ppm as a doublet ($J_{\text{H-H}}$: 1.65 Hz) assigned to H3 and H5 with another signal in 5.6 ppm as a triplet ($J_{1\text{H-H}}$: 1.38; $J_{2\text{H-H}}$: 1.74 Hz). In order to have a better view these contributions, Fig. 1 shows the ^1H NMR and their couplings, respectively.

The presence of only two hydrogen signal confirm the postulation of the high symmetry showed for this complex due the high magnetic equivalence displayed for the protons. Fig. 2 shows $^1\text{H}\{^{31}\text{P}\}$ NMR of the complex (**I**), a triplet at $\delta = 5.67$ ppm, corresponding to the H4 coupling with H3 and H5. Also we can observe a doublet at $\delta = 6.37$ ppm, which corresponds to one of the two protons H3 or H4 coupled to H5.

The $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3OD) (Fig. 3) shows only a intense doublet at $\delta = 45.44$ ppm with $J(\text{P-Rh}) = 152.8$ Hz characteristic of the TPPMS phosphine coupled with the CO ligand *cis* in the axial plane. It is interesting to

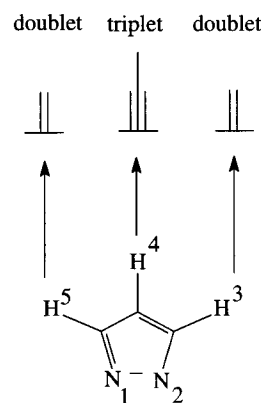


Fig. 1. Schematic representation of the pyrazol hydrogen.

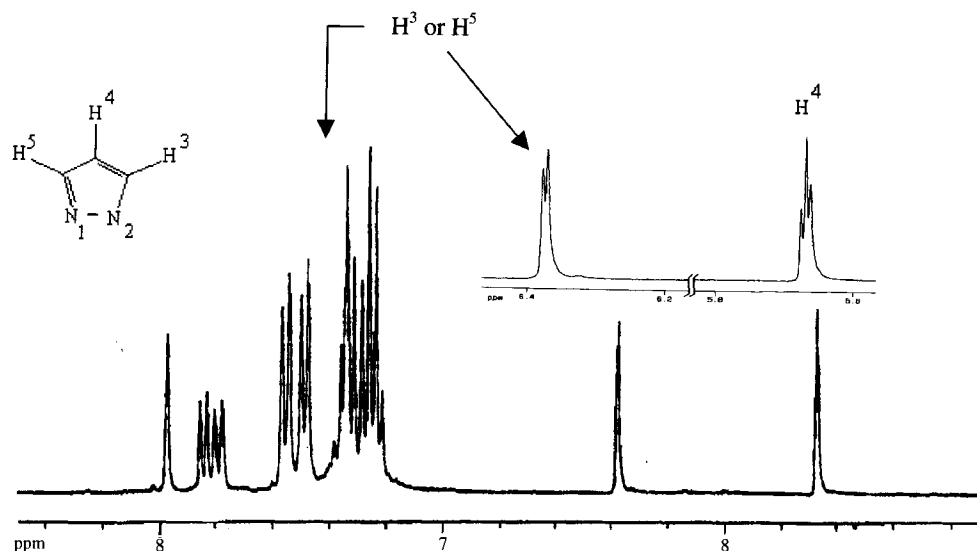


Fig. 2. $\{^{31}\text{P}\}^1\text{H}$ NMR of $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ in CD_3OD and under Argon.

mention that no signal corresponding to the free phosphine ($\delta = -5$ ppm) and the corresponding phosphine oxide ($\delta = 33$ ppm) were detected in the spectrum, confirming that this complex was achieved in a pure form, without any purification step, before running the corresponding catalytic experiments.

The FAB-MS spectrum shows a major peak at Z/e of 1124 au; $\text{I} = [\text{I} - \text{SO}_3 - \text{Na}]$ 1022.82 au; $[\text{I} + \text{Na SO}_3 \text{NaCO-H}]^-$ 1015 au; $[\text{I} + \text{CO} + 2\text{H}]$ 1098 au; $[\text{I} - \text{CO} - \text{SO}_3\text{Na} + 2\text{H}]^+$ 967 au; etc. From these spectroscopy evidences, we can assign a structure of a binuclear system bridged by two pyrazolate ligands. Each metal also has one TPPMS and one

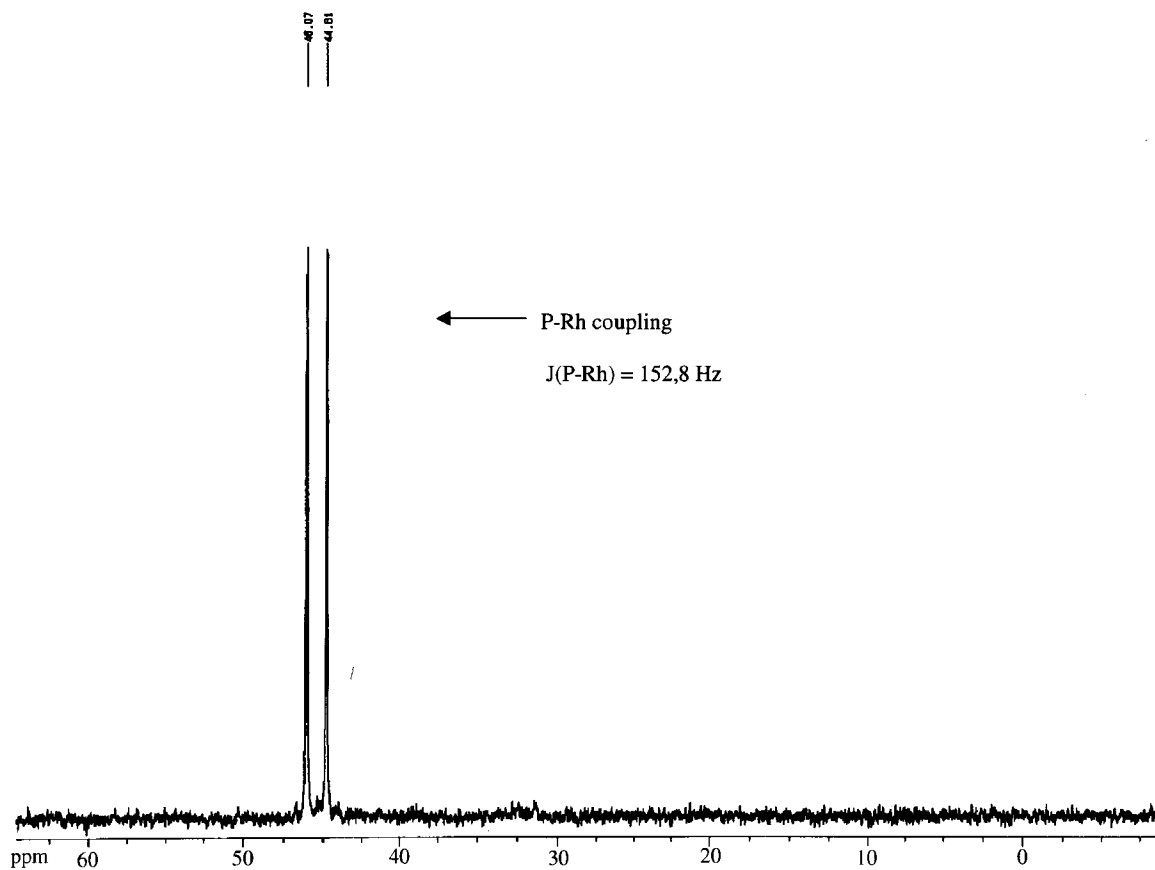


Fig. 3. ^{31}P NMR for the complex (I).

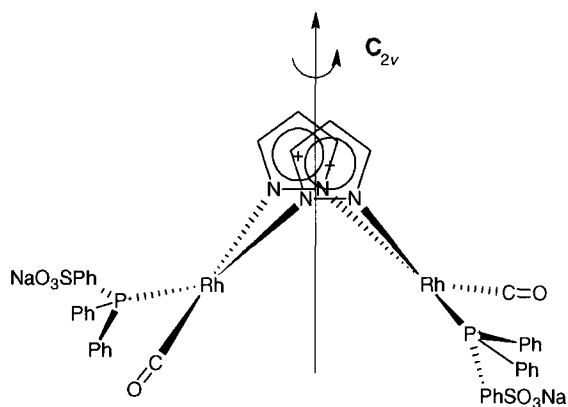


Fig. 4. Possible structure of $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ (**I**).

Table 1
Spectral data of $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$

Spectroscopic analysis	Assignment
FT-IR	In nujol: $\nu(\text{CO})$, 1975 cm^{-1}
$^1\text{H}\{^{31}\text{P}\}$ NMR	In pyrazolate: $\delta = 5.671 \text{ ppm}$; t, $-\text{H}^4$ $^1J(\text{H H}) = 1.38 \text{ Hz}$ $^2J(\text{H H}) = 1.74 \text{ Hz}$ $\delta = 6.370 \text{ ppm}$; d, $-\text{H}^3$ and $-\text{H}^5$ $J(\text{H H}) = 1.65 \text{ Hz}$ In TPPMS: $\delta = 7.232\text{--}7.969 \text{ ppm}$; m, aromatic character
^{31}P NMR	$\delta = 45.44 \text{ ppm}$; d, $J(\text{P-Rh}) = 152.8 \text{ Hz}$

Note: d: doublet, t: triplet, m: multiplett.

CO ligands bonded, according to the proposed structure as shown in Fig. 4.

However, by analogy with results obtained by other authors [14–16] for the Ph_3P analog complex, we conclude that complex (**I**) is a binuclear structure in which each rhodium atom has a square planar geometry with C_{2v} symmetry, similarly to the structure reported in the literature (Fig. 4).

The main absorption bands are summarized in Table 1.

3.2. Hydroformylation reactions

Complex **I** was previously used by us as a catalyst precursor in the water gas shift reaction and reduction of nitrobenzene [12]. The promising results obtained during that

Table 2

Distribution products of the hydroformylation of 1-hexene by $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2^a$

Time (h)	Total conversion (%)	Isomerization products (%)	2-Methyl-hexanal (%)	Heptanal (%)
1	33	95	2	3
2	54	88	6	6
5	85	84	8	8
8	94	75	13	12
12	99	61	19	20
24	99	30	29	41

^a $T = 90^\circ\text{C}$; $P = 15 \text{ atm}$ ($\text{CO} + \text{H}_2 = 1:1$); $[\text{Rh}] = 0.03 \text{ mmol}$; $\text{S/C} = 535:1$; $\text{P}/[\text{Rh}] = 0$; $\text{H}_2\text{O} = 20 \text{ ml}$; heptane = 18 ml.

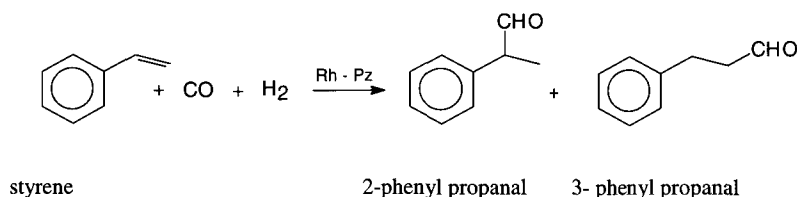
studies encourage us to investigate the catalytic behavior of this complex during the olefin carbonylation.

Thus, the hydroformylation experiments were conducted under the following initial conditions: a two-phase liquid system with water (20 ml) and heptane (18 ml), $P = 15 \text{ atm}$, $\text{CO}:\text{H}_2$ 1:1, $T = 90^\circ\text{C}$, $t = 16 \text{ h}$, substrate to catalyst ratio (S/C) = 535/1. The olefins investigated were 1-hexene and styrene which were tested in independent experiment by using the reaction conditions disclosed above. In Table 2, for the distribution products of the hydroformylation of 1-hexene, shows the total conversion and the distribution products during 24 h of reaction.

As shown in Table 2, complex (**I**) has a good activity for the olefin isomerization. We can infer that during the evolution of the reaction, terminal olefins are converted first and end up with the internal olefin (2-hexene, 3-hexene characterized by GC-MS) and in this way we can explain the formation of 2-methyl-hexanal as a hydroformylation product. At 12 h, equal quantities of 2-methyl-hexanal and heptanal are observed in the system and 60% of isomerization products are still present in the catalytic reaction. After 24 h, isomerization products are still present with n/i ratio of 1.3 similar to the value found for the analogue PPh_3 complex [8b].

It is interesting to note that similar observations were reported by Usón et al. [8a] for a series of binuclear rhodium–pyrazolate as catalytic precursors in a homogeneous medium, where no hydrogenation products were observed but an important isomerization reaction was found.

In the case of styrene, complex **I** only produces two products where according to Scheme 1, no product derivative of hydrogenation or isomerization product were observed in any of the experiment.



Scheme 1. Conversion of styrene to hydroformylation products (2-phenylpropanal and 3-phenylpropanal).

Table 3
Distribution products of the hydroformylation of styrene by $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})_2]_2^a$

Time (h)	Total conversion (%)	2-Phenylpropanal (%)	3-Phenylpropanal (%)
1	90	90	10
2	90	85	15
5	91	49	51
8	99	44	56
12	99	45	55
24	99	47	53

^a $T = 90^\circ\text{C}$; $P = 15\text{ atm}$ ($\text{CO} + \text{H}_2 = 1:1$); $[\text{Rh}] = 0.03\text{ mmol}$; $\text{S}/\text{C} = 522:1$; $\text{P}/[\text{Rh}] = 0$; $\text{H}_2\text{O} = 20\text{ ml}$; heptane = 18 ml.

The analysis of the product distribution shows the increase of the linear aldehyde and the decrease of the branched product as a function of time. During the first 4 h, the branched isomer (2-phenylpropanal) is found in larger proportion than the linear aldehyde (3-phenylpropanal). However, after 5 h of reaction, the system became in regimen and the linear proportion to branched aldehyde remains constant at least until the next 24 h of reaction, due to that the kinetics conditions control the formation of the hydroformylation products with a n/i ratio of 1:1 (Table 3).

In order to confirm that the hydroformylation reaction proceeds in a homogeneous phase, the mercury test was carried out in several independent experiments [17,18] and the results showed no interference at all with the evolution of the reaction. Also, the metal content in the organic phase was determined by atomic absorption analysis in each run. The results shows that <5 ppm was detected in the organic phase indicating that all of the metal remains in the aqueous phase.

A further series of experiments were carried out in order to investigate the effect of the variations of temperature, pressure and substrate to catalyst ratio in the hydroformylation of 1-hexene.

3.3. Temperature effect on the hydroformylation

The hydroformylation of 1-hexene was conducted at the reaction conditions previously stated. Initially, the tempera-

ture was varied from 60 to 140 °C. When the catalytic system was heated to temperatures higher than 100 °C, the solution showed evidences of decomposition due to the presence of a big amount of black particles suspended in a very dark catalytic solution the same observation described by Chaudhari and co-workers during the homogenous hydroformylation of 1-hexene, catalyzed by $\text{HRu}(\text{CO})(\text{PPh}_3)_3$ [19]. Below 90 °C, the conversion was very low with a big amount of isomerization products. For this reason, the temperature selected for the hydroformylation was set at 90 °C.

3.4. Pressure effect on the hydroformylation

The hydroformylation reaction of 1-hexene was carried out at pressures range from 5 to 25 atm at 90 °C. The conversion of 1-hexene to hydroformylation products, using the complex I as a catalytic precursor, seems to be independent of the gas pressure. In order to confirm this observation, a plot of $\log(\text{total conversion})$ versus $\log(\text{H}_2 + \text{CO})$ pressure (Fig. 5) shows a straight line with a slope equal to zero, which is evidence of the changes of the pressure does not affect the hydroformylation reaction. This results show that the reaction can be carried out in a wide range of $(\text{H}_2 + \text{CO})$ pressure and for the next experiment the value chosen was 20 bar of syngas.

3.5. The effect of the P/Rh ratio in the hydroformylation

In earlier reports [5], during the hydroformylation of 1-hexene by using rhodium-pyrazolate complexes in homogeneous system, it was observed that the P/Rh ratio has an influence in the activity and selectivity of the products. In this sense, some additional experiments were conducted in order to study the influence of the P/Rh ratio in the conversion of 1-hexene. Table 4 shows the effect of the P/Rh ratio variation.

As it is observed in Table 4, the conversion toward the hydroformylation products decreases as the P/Rh ratio increases. The explanation of this observation is due to the excess of TPPMS which promotes the CO elimination instead of the TPPMS elimination according to Scheme 2.

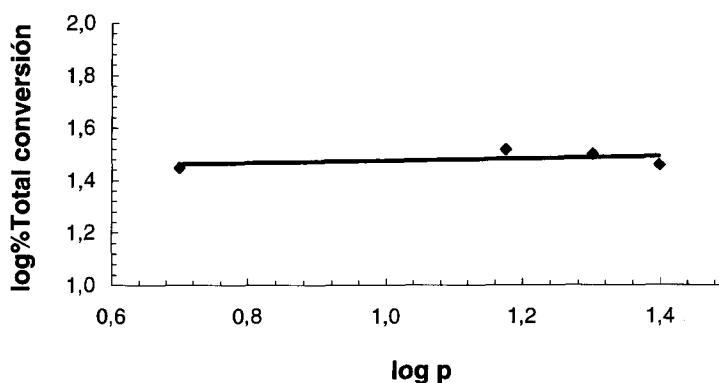
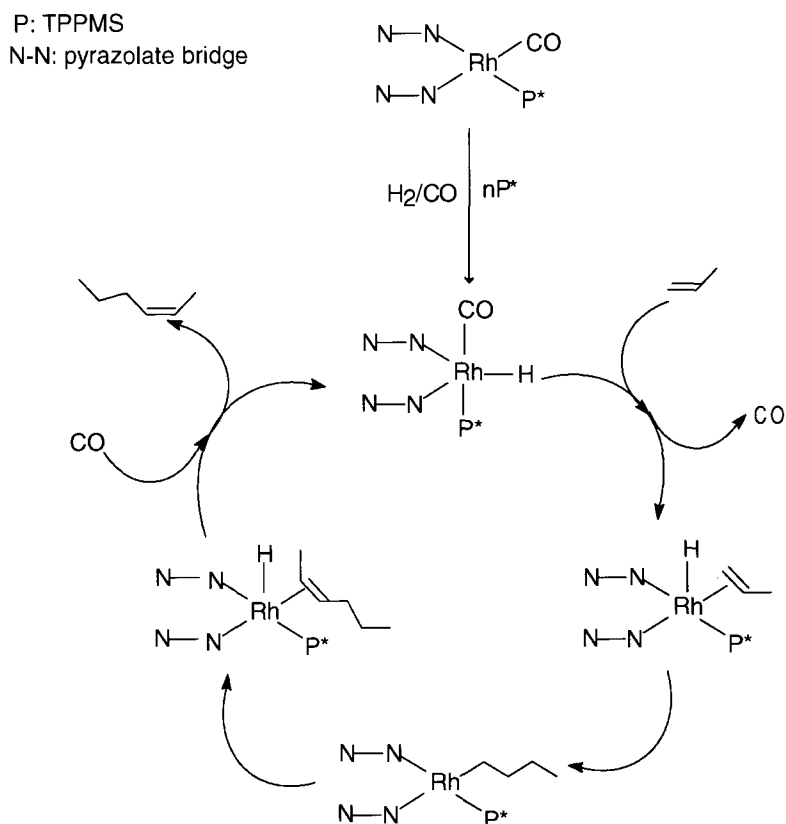


Fig. 5. Hydroformylation profile of 1-hexene linealized by pressure logarithm function.

Table 4
Distribution products of the hydroformylation of 1-hexene by $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ as a function of P/Rh ratio^a

P/[Rh]	Total conversion (%)	Isomerization products (%)	2-Methyl-hexanal (%)	Heptanal (%)
0	99	45	33	22
2	96	65	17	18
4	80	77	6	17

^a $T = 90^\circ\text{C}$; $t = 16\text{ h}$; $P = 15\text{ atm}$; $(\text{CO} + \text{H}_2 = 1 : 1)$; $[\text{Rh}] = 0.03\text{ mmol}$; $\text{S}/\text{C} = 535 : 1$; $\text{H}_2\text{O} = 20\text{ ml}$; heptane = 18 ml.



Scheme 2. Possible route for the olefin isomerization in the presence of the excess of TPPMS ligand.

In the presence of olefin it produced an intermediate olefin–Rh–H which suddenly promoted the olefin isomerization by alkene insertion into the M–H bond followed by β -hydride elimination [20].

3.6. Catalyst recycling

One very important aspect in catalysis is the capability of reusing the catalyst for a long period of time without major changes in the nature and activity of it. Taking into account this fact, it is necessary to obtain evidence about the recycling properties of the complex used in this work. In this sense, a set of experiment studying the stability of the complexes during the hydroformylation of 1-hexene was carried out in order to demonstrate the ability of this complex to catalyze this reaction. In this sense, four consecutive hydroformylation experiment were ran, *maintaining the same*

aqueous phase during the experiment and changing each after 24 h, the organic phase for another *fresh* phase which contains 1-hexene. The results obtained after this set of experiment can be seen in Table 5.

As shown in Table 5, this complex efficiently catalyzed the hydroformylation of 1-hexene after four experiments without major indications of dropping the activity. This

Table 5
Hydroformylation of 1-hexene by using the complex (I)^a

Run	Total conversion (%)
1	98
2	98
3	97
4	97

^a $T = 90^\circ\text{C}$; 1-hexene: $1.66 \times 10^{-3}\text{ mol}$; water, 20 ml; heptane, 18 ml; $t = 24\text{ h}$; $\text{S}/\text{C} = 535 : 1$; $P = 20\text{ atm}$; $(\text{CO} + \text{H}_2) = 1 : 1$.

experiment clearly shows the recycling capabilities of this type of catalyst precursor for the olefin hydroformylation.

4. Conclusions

The rhodium complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})_2]$ (**I**) was prepared and fully characterized using spectroscopic techniques. The great solubility in water of the complex (**I**) allows using it as catalyst precursor in the biphasic hydroformylation reaction of 1-hexene and styrene under mild reaction conditions.

During the 1-hexene hydroformylation, the result shows that this system promotes primarily the olefin isomerization and later the resulted aldehyde products with a low n/i ratio. High operation temperature produces decomposition of this complex and no significant effect is observed with the $\text{H}_2 + \text{CO}$ pressure. Moreover, the P/Rh ratio affects the selectivity to aldehydes promoting basically the olefin isomerization instead of the carbonylation.

When the complex is used in the hydroformylation of styrene, only two isomers, 2-phenylpropanal and 3-phenylpropanal, were detected with an increase of the selectivity to the linear isomer during the progress of the hydroformylation reaction. The complex **I** can be recycled several times without indication of loosing catalytic activity. Finally, no metal leaching is observed during the catalytic experiment. The mercury test for homogeneity in both systems showed that the biphasic catalytic systems has a molecular character.

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