Hydroformylation of Synthetic Naphtha Catalyzed by a Dinuclear *gem*-Dithiolato-Bridged Rhodium(I) Complex

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Abstract: This work focuses on the use of a *gem*-dithiolato-bridged rhodium(I) $[Rh_2(\mu\text{-}S_2CBn_2)(cod)_2]$ complex (cod = 1,5-cyclooctadiene, $Bn_2CS_2^{2-}$ = 1,3-diphenyl-2,2-dithiolatopropane) dissolved in toluene in the presence of monodentate phosphite P-donor ligand $(P(OPh)_3)$ under carbon monoxide/hydrogen (1:1, syngas) atmosphere as an effective catalyst for hydroformylation of some olefins (*oxo*-reactions). The capability of this system to catalyze the hydroformylation of hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene and their quaternary mixture (synthetic naphtha) has been demonstrated. This innovative method to perform the *in situ* hydroformylation of the olefins present in naphthas to oxygenated products would be a promissory work for a future industrial catalytic process applicable to gasoline improving based on *oxo*-reactions. An important observation is that variation of CO/H_2 pressure (6.8 − 34.0 atm), temperature (60 − 80 ºC), reaction time (2 − 10 h), rhodium concentration $((1.0 − 1.8)\times10^{-3}$ mol/L) affect hydroformylation reaction rates. Optimal conversion to oxygenated products were achieved under $[Rh] = 1.8 \times10^{-2}$ mol/L, $P(CO/H_2) = 34$ atm $(CO/H_2 = 1:1)$ at 80 ºC for 10 h.

Keywords: Homogeneous catalysis, syngas, naphtha, hydroformylation, olefins, *oxo*-reactions.

INTRODUCTION

The catalytic carbonylation of olefins in naphtha by *oxo* or Reppe type process [1-5] has been studied as an alternative route to conventional catalytic alkylation and hydrogenation processes [6-8]. Olefins are desirable for their octane value but are unwanted because they lead to deposits and gum formation and increased emissions of ozone forming hydrocarbons and toxic compounds [9]. Further, with the objective of increasing the octane content in the gasoline for improved emissions quality, diverse oxygenated additives like methyl *tert*-butyl ether (MTBE) or *tert*-amyl methyl ether (TAME) are commonly added in commercial gasoline [10]. Although, their use has been declined in response to environmental concerns. It has been found that MTBE easily pollutes large quantities of groundwater when gasoline is spilled or leaked at gas stations [11]. Therefore, there is a need to explore other oxygenated additives more environmentally benign. An alternative to this approach can be the *in situ* transformation of the olefins present in naphtha into oxygenated compounds with high added value, likes esters, aldehydes and acetals, among others, *via* catalytic carbonylation which it can be carried out in one step avoiding the expensive catalytic hydrogenation [1-5].

Accordingly, the *in situ* catalytic carbonylation of olefins from naphtha could be a promissory tool for the production of motor green-gasoline.

The synthesis of oxygenated organic products by reaction of an olefinic substrate with CO and H_2 (eq 1) in the presence of transition metal complexes is known as *oxo* reaction [12, 13]. This reaction, which was accidentally discovered by Otto Roelen in 1938, has received considerable attention [14, 15]. Although much progress has been made since then through the development of more efficient metal catalysts, hydroformylation continues to be the subject of innumerable studies, motivated by the need to increase the selectivity to linear or branched aldehydes, to reduce by-product formation, and to achieve milder and more environmentally friendly reaction conditions [16]. The homogeneous hydroformylation reaction is one of the oldest processes making use of soluble transition metal catalysts and it is one of the largest volumes of industrial applications of these catalysts [17].

linear or normal aldehyde (n)   branched or iso aldehyde (i)

(1)
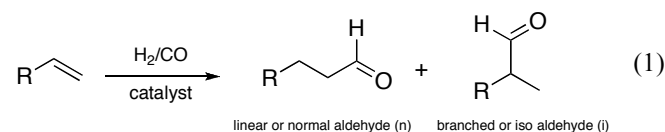
Mononuclear rhodium complexes are the most efficient catalysts for this reaction and, consequently, a great deal of work has been devoted to the improvement of rates and selectivities by ligand design [14, 18]. However, bimetallic

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catalysis has attracted considerable interest in recent years [19-25].

We have recently reported the synthesis of dinuclear rhodium complexes supported by *gem*-dithiolato ligands ($R_2CS_2^{2-}$) exhibiting a bridging and chelating coordination mode ($1:2\kappa^2S$, $1:2\kappa^2S'$) and a single bridgehead carbon atom between both sulphur atoms [26, 27]. Interestingly, the dinuclear *gem*-dithiolato bridged compounds [$Rh_2(\mu$-$S_2CR_2)(cod)_2$] (cod = 1,5-cyclooctadiene, R = Bn (benzyl), ^iPr; R_2 = -$(CH_2)_4$-,-$(CH_2)_5$-) dissolved in toluene in the presence of monodentate phosphine or phosphite P-donor ligands under carbon monoxide/hydrogen (1:1) atmosphere are efficient catalysts for the hydroformylation of oct-1-ene under mild conditions (6.8 atm of CO/H_2 and 80 ºC) [26, 28]. Interestingly, $P(OPh)_3$ (triphenyl phosphite) and $P(OMe)_3$ (trimethyl phosphite) resulted to be the best modifying ligands among the other phosphine (triphenylphosphine, trimethylphosphine, triisopropylphosphine or tricyclohexylphosphine) P-donor ligands used in these studies. Further, the system [$Rh_2(\mu$-$S_2CBn_2)(cod)_2$]/ $P(OPh)_3$ was tested in the hydroformylation-isomerization of *trans*-oct-2-ene (internal olefin). Under optimized conditions ($P(CO/H_2)$ = 13.6 atm at 100 ºC for 8 h, CO/H_2, 1/1; [Rh_2] = 1.0 mM, [*trans*-oct-2-ene]/[Rh_2] = 600) up to 64% of aldehyde selectivity and TOF(aldehyde) = 42 h^{-1} were obtained. These results show the moderate activity of this catalytic system for hydroformylation of internal double C-C bonds and this is an important property to take in account for naphtha hydroformylation. Naphtha contains large amount of internal olefin content (> 50%) [10].

One of the potential benefits of the *gem*-dithiolato-bridged rhodium(I) based system to be used as a catalyst for hydroformylation on naphtha is the presence of the sulfur containing dithiolato ligand. The deactivation of catalyst by organosulfur compounds present in the refinery cuts is one of the main concerns in the oil industry. However, Chuang *et al.* [29-31] employing supported rhodium catalyst Rh/SiO$_2$ and Baricelli *et al.* [25, 32] using a water-soluble rhodium complex [$Rh(\mu$-$Pz)(CO)(TPPTS)$]$_2$ (TPPTS = tris(*m*-sulfophenyl)phosphine trisodium salt and Pz = pyrazolate) reported that presence of sulfur in the media enhances the activity during hydroformylation reactions due to the formation of rhodium-sulfide species under the catalytic reaction conditions which could be responsible for the increase of the activity towards oxygenated products.

Additional potential advantages of the *gem*-dithiolato-bridged rhodium(I) system come from the structure and the coordination mode of the bridging ligand that produce much more rigid dinuclear systems with a smaller angle between the coordination planes of the rhodium centers and shorter Rh–Rh distances, which should favor the cooperative effects between the metal centers resulting in more active and selective catalysts than the monometallic systems. We report herein on the catalytic activity for the hydroformylation of some olefins present in naphtha by the *gem*-dithiolato dinuclear rhodium(I) [$Rh_2(\mu$-$S_2CBn_2)(cod)_2$] complex (Fig. **1**) in the presence of $P(OPh)_3$. The aim of this study is to determine the influence of the variation of some reaction parameters on reaction rates.
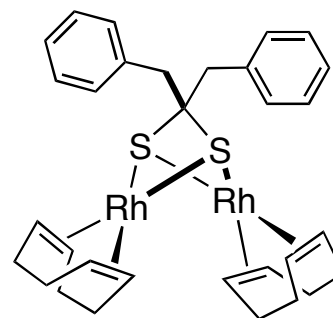

Fig. (1). Molecular structure of compound [$Rh_2(\mu$-$S_2CBn_2)(cod)_2$].

EXPERIMENTAL

Hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene, 2-methyl-pent-2-ene, toluene (Aldrich) were distilled prior to use. The gas He and the gas mixture CO/H_2 were purchased from BOC Gases and were used as received. The dinuclear rhodium complex [$Rh_2(\mu$-$S_2CBn_2)(cod)_2$] was prepared from $Bn_2C(SH)_2$ and [$Rh(\mu$-$OH)(cod)$]$_2$ following the procedure recently reported and their molecular structure determined by X-ray diffraction [27]. Analyses of liquid phase were done on a Buck Scientific 910 programmable gas chromatograph fitted with a MXT-1 (30 m x 0.52 mm x 1.0 mm) column and flame ionization detector, and using He as the carrier gas. A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) (30 m x 0.250 mm) column and a Varian Chrompack, Saturn 2000 mass selective detector were used to confirm the identity of the organic reaction products at the end of each run. Catalytic runs were performed in a 30 mL mechanically stirred and electrically heated stainless steel Parr reactor. In a typical run, 11.6 mg of the catalyst [$Rh_2(\mu$-$S_2CBn_2)(cod)_2$] (1.7×10^{-5} mol), 0.25×10^{-2} mol of olefin, 1.36×10^{-4} mol of $P(OPh)_3$ and 16 mL of toluene were added to the reaction vessel. The system was then flushed with nitrogen to remove the air and subsequently flushed with a portion of the mixture CO/H_2 (1:1) to remove all the nitrogen from the system. The reaction vessel was then charged with CO/H_2 (1:1) at the desired pressure (6.8 − 34.0 atm) and electrically heated to 60 − 80 ºC for 2 − 10 h. After a given time the reaction was stopped, the reactor cooled to room temperature, excess pressure was vented and the products were analyzed by GC and GC-MS techniques.

RESULTS

The catalytic carbonylation of each of the following olefins (Fig. **2**): hex-1-ene (terminal and linear olefin), cyclohexene (cyclic olefin), 2,3-dimethyl-but-1-ene (branched and terminal olefin) and 2-methyl-pent-2-ene (branched and internal olefin) was tested separately. These olefins were used as a model because they are generally present among other short-chain olefins in real naphtha [3, 5]. The results for the carbonylation of this four olefin-model system show that 2-methyl-pent-2-ene is the less reactive (Table **1**). For that reason, the studies for achieving optimal conditions (pressure of CO/H_2, temperature and reaction time) were the primary focus for this β-disubstituted olefin. The goal is to find the optimal conditions for the conversion

of this olefin which in principle could be the same for the rest of the individual olefins, for the quaternary system and for real naphtha. However, we want first to report the effects CO/H_2 molar ratio variation for the hex-1-ene under high pressure of $P(CO/H_2)$. Table **2** summarizes the data.
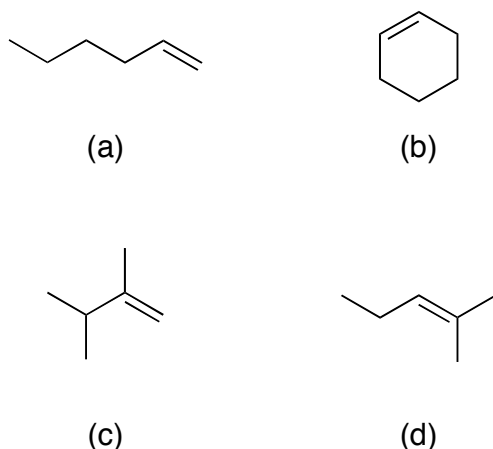
(a)

(b)

(c)

(d)

Fig. (2). Four olefin model for synthetic naphtha: hex-1-ene (**a**), cyclohexene (**b**), 2,3-dimethyl-but-1-ene (**c**) and 2-methyl-pent-2-ene (**d**).

Table 1. Hydroformylation of Olefins by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$] Catalyst[a]

Individual Components	Conversion (%)	Products (Selectivity,%)[b]
Hex-1-ene	(61)	Heptanal (75) 2-Methyl-hexanal (22)
2,3-Dimethyl-but-1-ene	(34)	3,4-Dimethyl-pentanal (83) 2,2,3-Trimethyl-butanal (15)
Cyclohexene	(25)	cyclohexanecarboxaldehyde (100)
2-Methyl-pent-2-ene	(15)	2,2-Dimethyl-pentanal (77) 2-Isopropyl-butanal (12) 3-Methyl-hexanal (8)

[a]Reaction conditions: [Rh$_2$] (1.7×10^{-5} mol, 1.0×10^{-3} mol/L), olefin (1×10^{-2} mol, 0.59 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36×10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 6.8 atm (CO/H$_2$, 1/1) at 80 ºC for 2 h.
[b]Selectivity for aldehyde formation = (ni/Σ ni)x100; ni = mmoles of product i; Σ ni = sum of all products; measured as areas in GC.

Table 2. CO/H$_2$ Molar Ratio Effects on Hydroformylation of Hex-1-Ene by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst[a]

CO/H$_2$ Molar Ratio	Conversion (%)
2:1	79
1:2	74
4:1	63
1:4	55

[a]Reaction conditions: [Rh$_2$] (1.7×10^{-5} mol, 1.0×10^{-3} mol/L), olefin (0.25×10^{-2} mol, 0.15 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36×10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) at 80 ºC for 2 h.

The results of the effect of varying the CO/H$_2$ pressure in the 6.8 − 34.0 atm range for the 2-methyl-pent-2-ene olefin system is summarized in Table **3**. From it can be observed

that an increase in the $P(CO/H_2)$ from 6.8 to 34.0 atm further increased the conversion values from 31 to 43%. Further optimization studies for the catalytic hydroformylation of the olefins will set the optimal value to $P(CO/H_2)$ = 34.0 atm.

Table 3. Carbon Monoxide/Hydrogen Pressure Effects on Hydroformylation of 2-Methyl-Pent-2-Ene by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P (OPh)$_3$ Catalyst[a]

CO/H$_2$ (atm)	Conversion (%)	Products (Selectivity,%)[b]
6.8	31	2,2-Dimethyl-pentanal (77) 2-Isopropyl-butanal (12) 3-Methyl-hexanal (6)
13.6	34	2,2-Dimethyl-pentanal (75) 2-Isopropyl-butanal (14) 3-Methyl-hexanal (7)
20.4	38	2,2-Dimethyl-pentanal (74) 2-Isopropyl-butanal (15) 3-Methyl-hexanal (7)
27.2	40	2,2-Dimethyl-pentanal (75) 2-Isopropyl-butanal (17) 3-Methyl-hexanal (5)
34.0	43	2,2-Dimethyl-pentanal (73) 2-Isopropyl-butanal (18) 3-Methyl-hexanal (4)

[a]Reaction conditions: [Rh$_2$] (1.7×10^{-5} mol, 1.0×10^{-3} mol/L), olefin (0.25×10^{-2} mol, 0.15 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36×10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), CO/H$_2$ (1/1) at 80 ºC for 2 h.
[b]Selectivity for aldehyde formation = (ni/Σ ni)x100; ni = mmoles of product i; Σ ni = sum of all products; measured as areas in GC.

The effect of varying the temperature in the 60 − 80 ºC range for the 2-methyl-pent-2-ene olefin system is summarized in Table **4**. This study was conducted in this temperature range because over 80 ºC some decomposition of the rhodium precursor is observed as was indicated by the color of the catalytic solutions [28]. Further, at temperatures below 60 ºC the conversion rate is slow. There is an increase on the conversion values from 27, 35 to 43% when the temperature is increased from 60, 70 to 80 ºC, respectively.

Table 4. Temperature Effects on Hydroformylation of 2-Methyl-Pent-2-Ene by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst[a]

Temperature (ºC)	Conversion (%)	Products (Selectivity,%)[b]
60	27	2,2-Dimethyl-pentanal (89) 2-Isopropyl-butanal (7) 3-Methyl-hexanal (1)
70	35	2,2-Dimethyl-pentanal (83) 2-Isopropyl-butanal (10) 3-Methyl-hexanal (3)
80	43	2,2-Dimethyl-pentanal (73) 2-Isopropyl-butanal (17) 3-Methyl-hexanal (5)

[a]Reaction conditions: [Rh$_2$] (1.7×10^{-5} mol, 1.0×10^{-3} mol/L), olefin (0.25×10^{-2} mol, 0.15 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36×10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) for 2 h.
[b]Selectivity for aldehyde formation = (ni/Σ ni)x100; ni = mmoles of product i; Σ ni = sum of all products; measured as areas in GC.

Table **5** is summarizes the effect of varying the reaction time in the 2 − 10 hours range for the 2-methyl-pent-2-ene

olefin system. The results show a steady increase in the conversion when increasing the reaction time, keeping constant the other reaction parameters, as well as constant product selectivity. These results suggest that under the range of time using in this study the catalytic system is stable.

Table 5. **Reaction Time Effects on Hydroformylation of 2-Methyl-Pent-2-Ene by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst[a]**

Reaction Time (h)	Conversion (%)	Products (Selectivity,%)[b]
2	43	2,2-Dimethyl-pentanal (73) 2-Isopropyl-butanal (18) 3-Methyl-hexanal (5)
4	54	2,2-Dimethyl-pentanal (74) 2-Isopropyl-butanal (16) 3-Methyl-hexanal (6)
6	57	2,2-Dimethyl-pentanal (72) 2-Isopropyl-butanal (17) 3-Methyl-hexanal (5)
10	76	2,2-Dimethyl-pentanal (75) 2-Isopropyl-butanal (14) 3-Methyl-hexanal (5)

[a]Reaction conditions: [Rh$_2$] (1.7x10^{-5} mol, 1.0x10^{-3} mol/L), olefin (0.25x10^{-2} mol, 0.15 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36x10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) at 80 ºC.
[b]Selectivity for aldehyde formation = (ni/Σ ni)x100; ni = mmoles of product i; Σ ni = sum of all products; measured as areas in GC.

The results from Tables **3-5** indicate that optimal conditions for the catalytic carbonylation of 2-methyl-pent-2-ene by the [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$] system are: P(CO/H$_2$) = 34 atm, CO/H$_2$ = 1:1, at 80 ºC for 10 h. Accordingly, these optimal values will be used to examine the catalytic conversion for the rest of the individual olefins. These results are shown in Table **6**.

Table 6. **Hydroformylation of the Four Individual Olefins by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst Under Optimized Conditions[a]**

Olefin	Conversion (%)	Products (Selectivity,%)[b]
Hex-1-ene	97	Heptanal (58) 2-Methyl-hexanal (39)
2,3-Dimethyl-but-1-ene	89	3,4-Dimethyl-pentanal (58) 2,2,3-Trimethyl-butanal (27)
Cyclohexene	93	cyclohexanecarboxaldehyde (100)
2-Methyl-pent-2-ene	67	2,2-Dimethyl-pentanal (76) 2-Isopropyl-butanal (18) 3-Methyl-hexanal (4)

[a]Reaction conditions: [Rh$_2$] (1.7x10^{-5} mol, 1.0x10^{-3} mol/L), olefin (1x10^{-2} mol, 0.59 mol/L), olefin/[Rh$_2$] = 600, P(OPh)$_3$ (1.36x10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) at 80 ºC for 10 h.
[b]Selectivity for aldehyde formation = (ni/Σ ni)x100; ni = mmoles of product i; Σ ni = sum of all products; measured as areas in GC.

The activity coming from carbonylation of a quaternary olefin mixture (composed by 43.0% of hex-1-ene, 23.7% of cyclohexene, 19.3% of 2,3-dimethyl-but-1-ene, and 14% of 2-methyl-pent-2-ene) by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$

catalyst system under the optimal conditions reported above are given in Table **7**.

Table 7. **Hydroformylation of the Quaternary Mixture of Olefins by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst[a]**

Total Conversion (%)	Individual Conversion (%)
	Hex-1-ene (90)
83	2,3-Dimethyl-but-1-ene (95)
	Cyclohexene (56)
	2-Methyl-pent-2-ene (67)

[a]Reaction conditions: [Rh$_2$] (1.7x10^{-5} mol, 1.0x10^{-3} mol/L), hex-1-ene (0.19x10^{-2} mol, 0.12 mol/L), cyclohexene (0.10x10^{-2} mol, 0.06 mol/L), 2,3-dimethyl-but-1-ene (0.08x10^{-2} mol, 0.05 mol/L, 2-methyl-pent-2-ene (0.06x10^{-2} mol, 0.04 mol/L), P(OPh)$_3$ (0.2 mL, 1.36x10^{-4} mol), P(OPh)$_3$/Rh = 4, olefin total volume (0.5 mL), toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) at 80 ºC for 10 h.

The results of the effect of rhodium concentrations variation on the (1.0 – 1.8)x10^{-3} mol/L range on the hydroformylation of the quaternary mixture of olefins by the [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ catalyst systems is summarized on Table **8**.

Table 8. **Rhodium Concentrations Effect on Hydroformylation of the Quaternary Mixture of Olefins by [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$]/P(OPh)$_3$ Catalyst[a]**

Amount of Catalyst (10^{-5} mol)	Total Conversion (%)	Individual Conversion (%)
1.70	80	Hex-1-ene (90) Cyclohexene (56) 2,3-Dimethyl-but-1-ene (99) 2-Methyl-pent-2-ene (67)
2.55	84	Hex-1-ene (96) Cyclohexene (60) 2,3-Dimethyl-but-1-ene (100) 2-Methyl-pent-2-ene (70)
3.00	87	Hex-1-ene (99) Cyclohexene (64) 2,3-Dimethyl-but-1-ene (100) 2-Methyl-pent-2-ene (72)

[a]Reaction conditions: hex-1-ene (0.19x10^{-2} mol, 0.12 mol/L), cyclohexene (0.10x10^{-2} mol, 0.06 mol/L), 2,3-dimethyl-but-1-ene (0.08x10^{-2} mol, 0.048 mol/L, 2-methyl-pent-2-ene (0.06x10^{-2} mol, 0.04 mol/L), P(OPh)$_3$ (1.36x10^{-4} mol), P(OPh)$_3$/Rh = 4, toluene (16 mL), P = 34 atm (CO/H$_2$, 1/1) at 80 ºC for 10 h.

DISCUSSION

The conversion (%) of olefins to carbonylated products for the individual olefins decreases in the order: hex-1-ene (61) > 2,3-dimethyl-but-1-ene (34) > cyclohexene (25) > 2-methyl-pent-2-ene (15), under the conditions given in Table **1**. The results for the carbonylation of this four olefins-model system show that 2-methyl-pent-2-ene is the less reactive and this order of reactivity concords with the reported by Ercoli [33] whom points that the mayor observed reactivity corresponds to α-olefins, followed by cyclic and by β-disubstituted olefins. In our system hex-1-ene and 2,3-

dimethyl-but-1-ene represent the α-olefins, cyclohexene represents the cyclic olefin and 2-methyl-pent-2-ene represents the β-disubstituted olefin. The same tendency was observed for the carbonylation of these four olefins catalyzed by [Rh(cod)(4-picoline)$_2$](PF$_6$) (cod = 1,5-cyclooctadiene) complex immobilized on poly(4-vinylpiridine) in contact with methanol under carbon monoxide atmosphere [7].

The hydroformylation of these model olefins catalyzed by *gem*-dithiolato-bridged rhodium(I) [Rh$_2$(μ-S$_2$CBn$_2$) (cod)$_2$]/ P(OPh)$_3$ system produces primarily aldehydes, in general low conversion to olefin isomers (3-5%) and without formation of alcohols and olefin hydrogenation products. Those observations confirm the high selectivity towards aldehydes by this Rh/P(OPh)$_3$ catalytic system. In the case of α-olefins both the linear and the branched aldehyde product were obtained due to the addition of the formyl group on either carbon double bond. For to β-olefin three aldehydes are observed, two are formed by the addition of the formyl group on either carbon double bond and the other due to the isomerization of olefin. In addition, as is shown in Table **1**, for hex-1-ene is observed that heptanal (linear isomer) represent 77% of the product composition whereas 2-methy-hexanal (branched isomer) represent 23% with *n/i* ratio of 3.35. Furthermore, 2,3-dimethyl-1-butene is converted to the lineal aldehyde; 3,4-dimethyl-1-pentanal in (84%) with low tendency for the isomer product; 2,2,3-trimethyl-butanal (16%). The cyclohexene is only converted to cyclohexanecarboxaldehyde (100%) and 2-methyl-pent-2-ene is converted to 2,2-dimethyl-pentanal (79%), 2-isopropyl-butanal (13%) and 3-methyl-hexanal (8%).

Table **2** shows that maximum conversion for hex-1-ene can be obtained at CO/H$_2$ molar ratio of 1:1. This value matches with the stoichiometric relationship required by eq. 1. Table **3** shows that the percentage of conversion of 2-methyl-pent-2-ene follows a linear dependence on [CO/H$_2$] in the range of the study. Based on this linear dependence we suggest a possible mechanism in that the rate-limiting step (k_2) is preceded by coordination of CO and H$_2$, e.g.

$$[Rh]+CO+H_2 \xrightarrow{k_1} [H_2\text{-Rh-CO}] \xrightarrow{k_2,\ olefin} \text{oxygenated products} \quad (2)$$
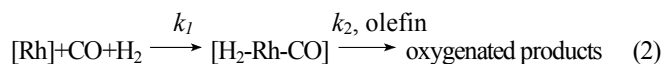
Further more, it can be seen that the variation of P(CO/H$_2$) changes the selectivity. Namely, it observed a slightly decrease for the selectivity toward 2,2-dimethyl-pentanal and 3-methyl-hexanal production from 77 to 73% and from 6 to 4%, respectively. There is also a slightly increase for 2-isopropyl-butanal production from 14 to 18%.

Table **4** shows that maximum conversion can be obtained at 80 ºC. Unfortunately, due to limitations related to the low thermal stability of the *gem*-dithiolato-bridged rhodium(I) complex at high temperatures and to its poor catalytic performance at low temperature was not possible to expand the range of the temperature over 80 ºC and below 60 ºC. An activation energy (Ea = 10.1 kJ/mol K) was calculated from an Arrhenius-type plot (Ln % of conversion *vs* 1/T). In addition, the variation of temperature changes the selectivity. It observed a decrease for the selectivity toward 2,2-dimethyl-pentanal production from 89 to 73% and an increase for 2-isopropyl-butanal and 3-methyl-hexanal production from 7 to 17% and from 1 to 5%, respectively.

Table **5** shows that the conversion gradually increases with extent of reaction time and the maximum value of 76% is

achieved in 10 h. There is an increase of 1.7-fold when the reaction time is changed from 2 to 10 h. However it is worth noting that the variation of reaction time does not change significantly the selectivity towards the three aldehyde products. This suggests that the catalytic ability of rhodium species formed under the catalytic reactions conditions towards the hydroformylation the 2-methyl-pent-2-ene in this time scale of study remains constant. Accordingly, the reaction rates for the formation of three products should keep a constant relationship, which is independent of the giving reaction time.

The data from Table **6** shown the expected increment of the olefin conversion of 1.6- (hex-1-ene), 2.6- (2,3-dimethyl-but-1-ene), 2.5- (cyclohexene) and 4.7-fold (2-methyl-pent-2-ene) under the optimal values for CO/H$_2$ molar ratio, pressure of CO/H$_2$, temperature and reaction time.

The data from Table **7** show that conversion (%) of olefins to aldehydes in the quaternary mixture (q.m.) decreases as: 2,3-dimethyl-but-1-ene (95) > hex-1-ene (90) > 2-methyl-pent-2-ene (67) > cyclohexene (56). This q.m. mixture is composed (wt.%) by 43.2% of hex-1-ene, 23.3% of cyclohexene, 19.4% of 2,3-dimethyl-but-1-ene, and 14.1% of 2-methyl-pent-2-ene. However, when the normalized conversion values (NCV)$_i$ for each of the four olefin in the mixture (Eq 3, [olefin$_i$]$_0$ = initial concentration of a given individual olefin(i), $\sum$ = summatory factor of the four olefins) the resulted order is: hex-1-ene (56.7) > 2,3-dimethyl-but-1-ene (11.4) > cyclohexene (10.1) > 2-methylpent-2-ene (4.7) for the total 83% conversion. It can be observed that the normalized conversion values fallow the order: α-olefins (hex-1-ene and 2,3-dimethyl-but-1-ene) > cyclic olefin (cyclohexane) > β-disubstituted olefin (2-methyl-pent-2-ene). The NCV values take in account the relation between the amounts of olefin in the mixture (define as wt.%) and their catalytic conversion values. These values represent the amounts of olefin converted if the mixture had the 1:1:1:1 composition expressed in wt.%. Obviously, the lesser the amount of the olefin in the mixture the faster is its consumption for a given time.

$$NCV_i = \frac{w.t.\%(olefin_i\ in\ q.m.) \times \left[olefin_i\right]_0}{\sum_i w.t.\%(olefin_i\ in\ q.m.) \times \left[olefin_i\right]_0} \times \%conv.\ olefin_i \quad (3)$$

The results from Table **8** show a moderate increase for the total conversion from 80% at [Rh] = 1.0x10^{-3} mol/L to 87% at [Rh] = 1.8x10^{-3} mol/L. Furthermore, the individual conversion for each olefin also increases. Namely, conversion of hex-1-ene increases from 90% to 99%, conversion of cyclohexene increases from 56% to 64%, conversion of 2,3-dimethyl-but-1-ene increases from 99% to 100% and conversion of 2-methyl-pent-2-ene increases from 67% to 72% under the conditions described in Table **8**.

CONCLUSIONS

The results of the investigation herein performed on the *gem*-dithiolato-bridged rhodium(I) [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$] catalysts pointed out the following main conclusions: The *gem*-dithiolato-bridged rhodium(I) [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$] in the presence of (P(OPh)$_3$) under carbon monoxide/hydrogen atmosphere shows catalytic carbonylation activity for hex-1-ene, cyclohexene, 2-methyl-pent-2-ene and 2,3-dimethyl-but-2-ene, also for the quaternary mixtures of these substrates (synthetic naphtha) under the condition studied. The principal carbonylated products obtained are aldehydes. In synthetic

naphtha conversion, the best performance was obtained under the following reactions parameters: [Rh] = 3.40x10^{-5} mol, [P(OPh)$_3$] = 1.36x10^{-4} mol, P(CO/H$_2$) = 34 atm, CO/H$_2$ =1:1 at 80 ºC for 10 h. The results summarized above confirmed that the catalytic carbonylation of olefins present in synthetic naphtha performed through operating strategy based on *oxo* type process might have potential benefice effects on olefin abatement and *in situ* oxygenated products formation in the same step for improving the quality of gasoline.

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