

## Hydroformylation of synthetic naphtha catalyzed by *gem*-dithiolato-bridged rhodium complexes

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### Introduction

The products coming from the catalytic carbonylation reactions of C6-C8 olefins by soluble [1] and immobilized transition metal complexes [2] offer access to wide range of important oxygenated compounds which could be used in a though be future industrial catalytic process for gasoline improving based on *in situ* carbonylation reaction over olefins present in naphtha.

The reaction of  $[\text{Rh}(\mu\text{-OH})(\text{cod})_2]$  (cod = 1,5-cyclooctadiene) with 1,3-diphenyl-2,2-dimercaptopropane ( $\text{CBn}_2(\text{SH})_2$ ) yields the *gem*-dithiolato-bridged compound  $[\text{Rh}_2(\mu\text{-S}_2\text{CBn}_2)(\text{cod})_2]$  [3,4]. This compound dissolved in toluene in the presence of  $\text{P}(\text{OPh})_3$  and under carbon monoxide/hydrogen (1:1) atmosphere, is an effective catalyst for the hydroformylation of quaternary mixture of hex-1-ene (43 wt.%), cyclohexene (23 wt.%), 2,3-dimethyl-but-1-ene (20 wt.%) and 2-methyl-pent-2-ene (14 wt.%) (synthetic naphtha). The four olefins are transformed in linear and branched aldehydes as major products, and minor amounts of products coming from the isomerization of the starting substrates.

### Materials and Methods

Hex-1-ene, cyclohexene, 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene (Aldrich) were distilled prior to use. 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 ( $1.7 \times 10^{-5}$  mol),  $1 \times 10^{-2}$  mol of olefin,  $1.36 \times 10^{-4}$  mol of  $\text{P}(\text{OPh})_3$  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 carbon monoxide to remove all the nitrogen from the system. The reaction vessel was then charged with  $\text{CO}/\text{H}_2$  at the desired pressure (6.8 - 34.0 atm) and electrically heated to 60 - 80 °C for 2. 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 and Discussion

The conversion (%) of olefins to aldehydes products decreases in the order: 2,3-dimethyl-but-1-ene (78) > hex-1-ene (71) > 2-methyl-pent-2-ene (44) > cyclohexene (36), under the following conditions  $[\text{Rh}] = 1.7 \times 10^{-5}$  mol,  $\text{P}(\text{OPh})_3 = 1.36 \times 10^{-4}$  mol,  $\text{P}(\text{OPh})_3/\text{Rh} = 4$ , toluene = 16 mL,  $[\text{olefin}] = 1 \times 10^{-2}$  mol,  $[\text{olefin}]/[\text{Rh}] = 300$  molar ratio under 500 psi of  $\text{CO}/\text{H}_2$  at 80 °C for 2 h. However, the values of the relation (wt. % of the individual olefin on the quaternary mixture/% of conversion) for the individual olefins follows as cyclohexene (0.63) > hex-1-ene (61) > 2-methyl-pent-2-ene (0.32) > 2,3-dimethyl-but-1-ene (0.26). The results for the carbonylation of this four olefin-model system show that 2,3-dimethyl-but-1-ene and 2-methyl-pent-2-ene are the less reactive.

An increase in the  $\text{P}(\text{CO}/\text{H}_2)$  from 6.8 to 13.6, to 20.9, to 27.2 and to 34.0 atm further increased the carbonylation overall yield (%) value from 38 to 42 to 49 to 57 and to 60%, respectively. These finding indicate that catalyst activity for the carbonylation reaction follows a linear dependence on  $[\text{CO}/\text{H}_2]$  in the range of study and suggests the formation of hydride-carbonyl-rhodium species followed by slower step to give organic products.

An increase in temperature from 60 to 70 and to 80 °C further increased the carbonylation overall yield (%) value from 47, to 53 and to 60%, respectively. These results show that reaction follows a linear dependence on 60–80 °C range at  $\text{P}(\text{CO}/\text{H}_2) = 34.0$  atm, suggesting the intervention of the Rh catalytic active species with the same nuclearity.

An increase in the reaction time from 2 to 4 to 6 to 8 and to 10 h increased the carbonylation overall yield (%) value from 60 to 65 to 70 to 76 and to 80%, respectively. The results show a positive effect on the carbonylation of the olefin catalytic activities with the increases of reaction time in the 2–10 h range at  $\text{P}(\text{CO}/\text{H}_2) = 34$  atm at 80 °C.

### Significance

In this work we carried out the catalytic transformation of synthetic naphtha, in oxygenated compounds (aldehyde) under  $\text{CO}/\text{H}_2$  atmosphere and these results constitutes a promissory work for a future industrial catalytic process for gasoline improving based on hydroformylation reactions.

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