

RKCL5309

## HYDROFORMYLATION REACTIONS OF THE *trans*-Mo(CO)<sub>4</sub>(*p*-C<sub>5</sub>NH<sub>4</sub>SO<sub>3</sub>NA)<sub>2</sub> COMPLEX IN BIPHASIC MEDIUM

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*Received October 1, 2007, in revised form February 18, 2008, accepted March 12, 2008*

### Abstract

*Trans*-bis(sodium pyridine-*p*-sulphonate)tetracarbonylmolybdenum(0) complex, (*trans*-Mo(CO)<sub>4</sub>(*p*-PySO<sub>3</sub>Na)<sub>2</sub>, (1)) was used as a catalytic precursor for the 1-hexene hydroformylation reaction, in biphasic toluene/water medium (T = 100°C, syngas total pressure = 600 psi, p<sub>H<sub>2</sub></sub>/p<sub>CO</sub> = 1). Complex (1) showed good activity favoring the linear aldehyde. Likewise as other organic olefin substrates and with synthetic and real naphtha, good conversions to oxygenated products were obtained.

*Keywords:* Biphasic catalysis, hydroformylation, naphtha, molybdenum complex

## INTRODUCTION

Biphasic catalysis is a useful tool in modern industrial chemistry, with organic solvent substitution, catalysis reuse, better product separation, or use of water as solvent as strategies for cleaner processes and less energy use. Recently, the use of water-soluble transition metal complexes with sulphonated

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phosphine ligands has increased [1-2]. For example, water soluble rhodium complexes have been used in the hydroformylation of propene [3-6], oleic alcohol, 1-octene and dicyclopentadiene hydroformylation [7] and a review article describes aqueous biphasic hydroformylation with rhodium complexes [8]. Recently, we reported olefin and naphtha hydroformylation using mononuclear rhodium complexes with water soluble phosphines [9-10], and with molybdenum complexes [11]. Here we report olefin and refinery naphtha hydroformylation with *trans*-Mo(CO)<sub>4</sub>(*p*-PySO<sub>3</sub>Na)<sub>2</sub> (**1**) in a toluene/water biphasic medium.

## EXPERIMENTAL

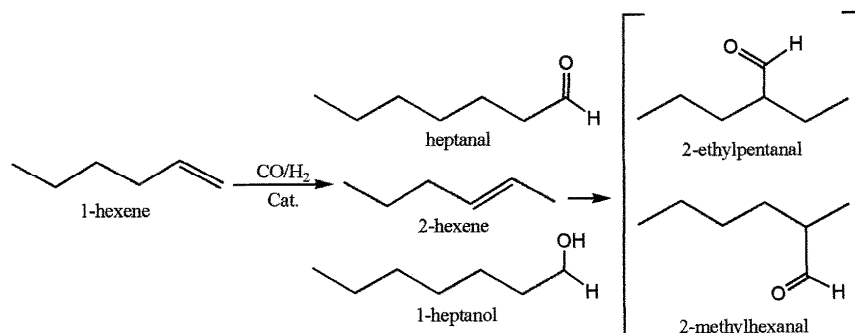
### Materials and methods

*Reagents:* CO, H<sub>2</sub> and Ar (Gases Industriales de Venezuela) were obtained commercially and used as received. The liquid substrates used in catalysis were distilled before use; EtOH, toluene and H<sub>2</sub>O were purified as described in the literature [12]. A real naphtha cut used was from the El Palito refinery, Venezuela. The *trans*-Mo(CO)<sub>4</sub>(*p*-PySO<sub>3</sub>Na)<sub>2</sub> (**1**) complex used in the catalytic runs is prepared as reported in [1].

*Catalytic trials:* Catalytic trials were done in a 125 mL Parr reactor with an internal glass liner, heating unit, temperature and stirring control, and a sampling valve. Conditions for a typical trial were: toluene (30 mL), H<sub>2</sub>O (30 mL), olefin or olefin mixtures (1 mL), Mo complex (4 mg, 0.07 mmol), substrate/catalyst = *ca.* 1000:1, H<sub>2</sub> pressure (300 psi), CO pressure (300 psi), temperature (50°C - 120°C), 1600 rpm stirring rate to ensure thorough mixing and emulsion formation, 4 h reaction time. Reaction products were analyzed in a PE, Autosystem GC, using a 3 m column (0.6 cm diameter) of 10% tricresyl phosphate on Cromosorb P (80 - 100 mesh), with H<sub>2</sub> carrying gas and a TC detector.

## RESULTS AND DISCUSSION

*1-hexene hydroformylation with complex (1).* 1-hexene was selected as a model olefin substrate; the possible oxygenated reaction products are shown in Scheme 1. As the reaction progresses (see Table 1), OXO products are produced, favoring the terminal aldehyde that reaches 50% selectivity at the end of the reaction. The other important product is the internal aldehyde expected from the terminal olefin (38% selectivity after 240 min). Minor products are the terminal alcohol, and with 8% selectivity to the aldehyde derived from the 2-hexene isomerization product.

**Scheme 1.** 1-hexene hydroformylation principal products**Table 1**

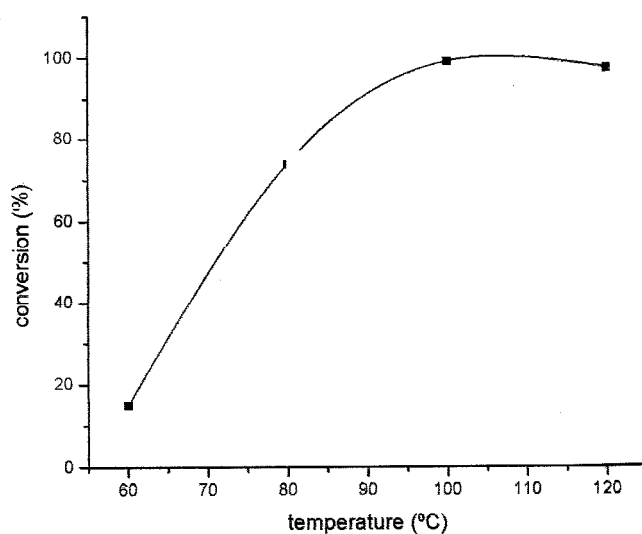
1-hexene hydroformylation with complex (1). Time effect

| Time (min) | % Conversion OXO products | Selectivity(%)   |                  |          |            |
|------------|---------------------------|------------------|------------------|----------|------------|
|            |                           | 2-Ethyl-pentanal | 2-Methyl-hexanal | Heptanal | 1-Heptanol |
| 30         | 13                        | 2                | 4                | 7        | 0          |
| 60         | 27                        | 2                | 6                | 17       | 2          |
| 90         | 78                        | 3                | 27               | 45       | 3          |
| 120        | 91                        | 5                | 36               | 47       | 3          |
| 150        | 93                        | 6                | 37               | 47       | 3          |
| 180        | 96                        | 7                | 37               | 49       | 3          |
| 210        | 100                       | 8                | 38               | 50       | 4          |
| 240        | 100                       | 8                | 38               | 50       | 4          |

(1-hexene: 1.0 mL toluene: 30 mL water: 30 mL catalyst: 4 mg, total pressure: 600 psi,  $P_{\text{CO/H}_2} = 1/1$ , 1600 rpm stirring, T: 100°C; 4 h total reaction time)

*1-hexene hydroformylation with complex (1) Temperature effect:* The OXO products increase with temperature (see Fig. 1 and Table 2), reaching a maximum at 100°C, with a product distribution explained previously, favoring the terminal aldehyde. There is little reaction below 60°C, and the slight decrease at 120°C, could be due to the decomposition of complex (1).

*1-hexene hydroformylation with complex (1) Total pressure effect:* The % conversion to OXO products increases with higher total syngas pressures ( $p_{CO}/p_{H_2} = 1$ ) (see Fig. 2 and Table 3). At 900 psi, the conversion is almost complete, favoring the terminal aldehyde (near 52%), with less internal aldehyde (near 37%) and a small proportion of other products.



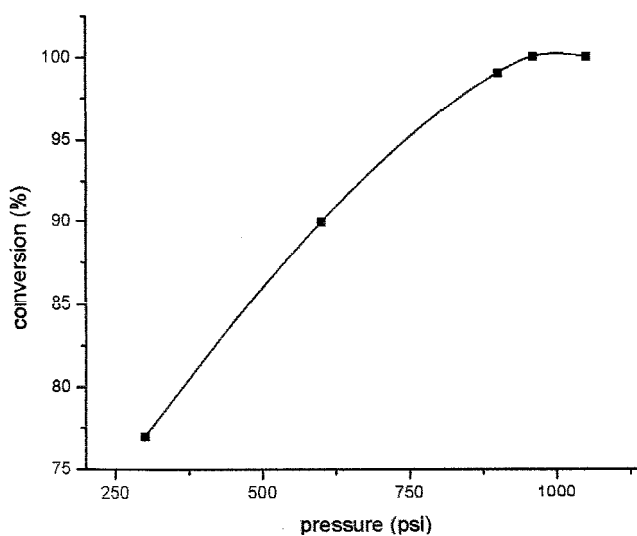
**Fig. 1.** 1-hexene hydroformylation with complex (1). Temperature effect (1-hexene: 1.0 mL, toluene: 30 mL, water: 30 mL, catalyst: 4 mg, 4 h reaction time, total pressure: 600 psi,  $P_{CO/H_2} = 1/1$ , 1600 rpm stirring)

**Table 2**

1-hexene hydroformylation with complex (1). Temperature effect

| Temperature (°C) | % Conversion OXO products | Selectivity (%)  |                  |          |            |
|------------------|---------------------------|------------------|------------------|----------|------------|
|                  |                           | 2-Ethyl-pentanal | 2-Methyl-hexanal | Heptanal | 1-Heptanol |
| 60               | 15                        | 3                | 5                | 6        | 1          |
| 80               | 74                        | 5                | 26               | 40       | 3          |
| 100              | 100                       | 8                | 36               | 53       | 3          |
| 120              | 97                        | 7                | 35               | 52       | 2          |

(1-hexene: 1.0 mL toluene: 30 mL water: 30 mL catalyst: 4 mg, total pressure: 600 psi,  $P_{CO/H_2} = 1/1$ , 1600 rpm stirring; 4 h reaction time)



**Fig. 2.** 1-hexene hydroformylation with complex (**1**). Total pressure effect. (1-hexene: 1.0 mL, toluene: 30 mL, water: 30 mL, catalyst: 4 mg, 4 h reaction time,  $P_{\text{CO}/\text{H}_2} = 1/1$ , 1600 rpm stirring, T: 100°C)

**Table 3**

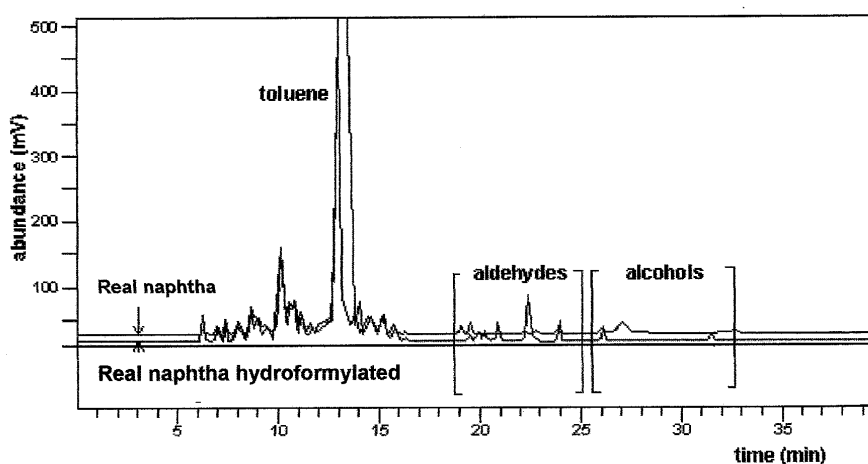
1-hexene hydroformylation with complex (**1**). Total pressure effect

| Pressure (psi) | % Conversion OXO products | Selectivity (%)  |                  |          |          |
|----------------|---------------------------|------------------|------------------|----------|----------|
|                |                           | 2-Ethyl-pentanal | 2-Methyl-hexanal | Heptanal | Heptanol |
| 300            | 77                        | 4                | 25               | 45       | 3        |
| 600            | 90                        | 5                | 35               | 47       | 3        |
| 900            | 99                        | 6                | 37               | 52       | 3        |
| 1000           | 100                       | 7                | 37               | 52       | 4        |
| 1100           | 100                       | 7                | 37               | 52       | 4        |

(1-hexene: 1.0 mL, toluene: 30 mL, water: 30 mL, catalyst: 4 mg,  $P_{\text{CO}/\text{H}_2}=1/1$ , 1600 rpm stirring, T: 100°C; 4 h reaction time)

*Hydroformylation of other organic substrates with complex (1):* The reaction products are given in Table 4. The catalytic precursor, complex (**1**), shows good

selectivity for OXO products, favoring terminal olefins, but giving the expected aldehydes and alcohol products even for the crowded olefins. The observed reactivity, under similar reaction conditions, is the following: 1-hexene > cyclohexene > 2-methyl-2-pentene > 2,3-dimethyl-2-butene. Similar results are observed with binary olefin mixtures. An important problem in the petroleum industry is the high olefin contents in commercial naphthas, mostly compounds with six carbons atoms, that need to be converted to alkanes through catalytic conversion, and also the need to add oxygenated compounds to improve fuel quality. This problem has been investigated with organometallic complexes in carbonylation reactions [9-10]. A synthetic naphtha (approximate volume composition: 1-hexene 32,0%, cyclohexene 11,4%, 2-methyl-2-pentene 28,3% and 2,3-dimethyl-2-butene 28,3%) was tried under similar reaction conditions, giving a 52% conversion with good selectivity for oxygenated products. Hydroformylation of a 1-hexene/thiophene = 1 mixture shows only a slight activity decrease, indicating that complex (1) or other intermediates derived from it, are resistant to poisoning by sulfur compounds, normally present in real naphthas.



**Fig. 3.** Real naphtha hydroformylation with complex (1). (Naphtha: 1.0 mL, toluene: 30 mL, water: 30 mL, catalyst: 4 mg, 4 h reaction time, total pressure: 600 psi,  $P_{\text{CO}/\text{H}_2} = 1/1$ , 1600 rpm stirring, T: 100°C; chromatogram: abundance (mV) vs retention time (min))

The separated water layer containing the Mo complex (UV-Vis spectra monitored, under Ar) can be recycled at least four times without apparent loss in the catalytic activity. Test reactions in the presence of liquid mercury do not show any significant activity changes, indicating that metallic molybdenum is not the catalytic phase.

**Table 4**

1-hexene and other organic substrates hydroformylation with complex (1)

| Substrate                                     | Conversion (%) | Selectivity (%)   |
|---|----------------|---|
| 1-hexene                                      | 95             | heptanal (47) 2-methylhexanal (36)<br>2-ethylpentanal (8) 1-heptanol (4)  |
| 1-hexene/thiophene (1/1)                      | 85             | heptanal (45) 2-methylhexanal (34)<br>2-ethylpentanal (4) 1-heptanol (2)  |
| cyclohexene                                   | 78             | cyclohexanecarbaldehyde (40)<br>cyclohexylmethanol (38)   |
| 2-methyl-2-pentene                            | 50             | 2,2-dimethylpentanal (35)<br>2,2-dimethylpentanol (15)  |
| 2,3-dimethyl-2-butene                         | 8              | 2,2,3-trimethylbutanal (6)<br>2,2,3-trimethylbutanol (2)  |
| 1-hexene/cyclohexene): 1/1                    | 85             | heptanal (35) 2-methylhexanal (28)<br>2-ethylpentanal (9) 1-heptanol (4)<br>cyclohexanecarbaldehyde (5)<br>cyclohexylmethanol (4)   |
| 2-methyl-2-pentene/2,3-dimethyl-2-butene: 1/1 | 56             | 2,2-dimethylpentanal (36)<br>2,2-dimethylpentanol (13)<br>2,2,3-trimethylbutanal (5)<br>2,2,3-trimethylbutanol (2)  |
| synthetic naphtha                             | 52             | 2-ethylpentanal (5) 2-methylhexanal (12)<br>heptanal (16) 1-heptanol (3)<br>cyclohexanecarbaldehyde (1)<br>cyclohexylmethanol (3) 2,2-dimethylpentanal (8)<br>2,2,3-trimethylbutanal (1) 2,2,3-trimethylbutanol (3) |

(Substrate: 1.0 mL, toluene: 30 mL, water: 30 mL, catalyst: 4 mg, total pressure: 600 psi,  $P_{CO/H_2}$  = 1/1, 1600 rpm stirring, T: 100°C; 4 h reaction time)

Conversion (%): percent conversion

*Real naphtha hydroformylation:* One of the goals of this study is to apply hydroformylation conditions with a molybdenum complex for real naphtha in order to reduce at least partially the olefin content, and produce oxygenated compounds “*in situ*” that improve gasoline formulations. The results are shown in Fig. 3, where the chromatograms for the real naphtha before and after the hydroformylation reaction are compared. There is evidence for aldehyde production (C6 and C7 aldehydes, 20 to 25 min retention times) and alcohols (longer retention times).

## CONCLUSIONS

Complex (**1**) has been tried as catalytic precursor in hydroformylation reactions in biphasic toluene/water mixtures, giving the expected OXO products, favoring the linear aldehyde and some alcohols, and reactivity order as: 1-hexene > cyclohexene > 2-methyl-2-pentene > 2,3-dimethyl-2-butene; also for binary olefin mixtures, a synthetic and real naphtha. The water catalyst layer can be reused at least four times without an activity loss, and the complex is resistant to thiophene poisoning. The reaction with real naphtha shows promising results that could be used to improve gasoline quality.

**Acknowledgement.** To CDCHT-ULA for financial support (Project C-1252-04-08-A).

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