Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Organometallic Chemistry 689 (2004) 3782–3792

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Rhodium-catalyzed hydroformylation of C6 alkenes and alkene mixtures – a comparative study in homogeneous and aqueous-biphasic media using PPh_3, TPPTS and TPPMS ligands

P.J. Baricelli [a,*], E. Lujano [a], M. Modroño [a], A.C. Marrero [a], Y.M. García [b], A. Fuentes [b], R.A. Sánchez-Delgado [b,*]

[a] Centro de Investigaciones Químicas, Facultad de Ingeniería, Universidad de Carabobo, Valencia, Venezuela
[b] Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Caracas, Venezuela

Received 17 May 2004; accepted 28 June 2004
Available online 5 August 2004

Abstract

The complexes $RhH(CO)L_3$, where L = PPh_3, $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS), and $(C_6H_5)_2P(m\text{-}C_6H_4SO_3Na)$ (TPPMS) were used as catalyst precursors for a comparative study of the catalytic hydroformylation of several C6 alkenes and alkene mixtures under moderate reaction conditions in homogeneous (PPh_3) and aqueous-biphasic (TPPTS, TPPMS) media. The biphasic systems are efficient for the hydroformylation of hex-1-ene, 2,3-dimethyl-1-butene, styrene, cyclohexene, and mixtures thereof, in water/*n*-heptane at 80 °C. The main problem associated with these catalysts is their tendency to promote alkene isomerization if the effective syngas concentration in the liquid phases is low, but this side-reaction can be suppressed by using higher CO/H_2 pressures (54 atm). The selectivity of both water-soluble catalysts for linear products of hex-1-ene and for branched products of styrene is modest in comparison with the homogeneous system, which may limit their utility for classical oxo uses, but this is not a disadvantage for other interesting applications related to the hydroformylation of alkene mixtures and particularly to naphtha upgrading where linear and branched products are equally useful. The catalysts can be recycled without significant loss of activity and are resistant to the presence of benzothiophene in the mixture.

Keywords: Hydroformylation; Rhodium; Phosphines; Aqueous biphasic catalysis

1. Introduction

The rhodium-catalyzed hydroformylation of alkenes continues to attract considerable attention because of its fundamental and applied interests. The chemistry associated with this reaction is rich and complex and despite the fact that it has been extensively studied, many fundamental challenges in catalyst design remain open. Hydroformylation is no doubt one of the most important industrial applications of transition metal complex-catalyzed reactions, with a current world production of over 6 million Tons of aldehydes and alcohols *per annum* [1,2].

Although industrial hydroformylation is carried our predominantly in homogeneous phase, new technologies have emerged in order to overcome the difficulties in the separation of the products from the catalysts and in the recycling of expensive noble metals at the end of the reaction. A particularly important alternative is the aqueous-biphasic version of the process in which the catalyst is immobilized in an aqueous phase that is immiscible with the phase containing the organic substrates and products [3,4]. This allows an easy and efficient recycle of the

---

[*] Corresponding authors. Tel.: +58-212-504-1741; fax: +58-212-504-1350.
E-mail address: rsanchez@ivic.ve (R.A. Sánchez-Delgado).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.06.051

catalyst and it has been used with great success in the Ruhrchemie/Rhone–Poulenc process, which is applied mainly to the hydroformylation of propylene to butyraldehyde and, to a lower extent, of C4 alkene mixtures to the corresponding aldehydes [1–4]. The Rh-derived catalyst employed in that process is solubilized in water through the use of triarylphosphine ligands modified by introducing highly polar sulfonate groups in the phenyl rings attached to phosphorus, specifically, the sodium salt of tris[(*meta*-sulfonato)phenyl]phosphine $P(m\text{-}C_6H_4SO_3Na)_3$, also known as triphenylphosphine trisulfonate (TPPTS) [3,4]. For longer-chain alkenes (C5+), Union Carbide has proposed a process involving Rh together with the sodium salt of [(*meta*-sulfonato)phenyl]diphenylphosphine $Ph_2P(m\text{-}C_6H_4SO_3Na)$, (triphenylphosphine monosulfonate, TPPMS), or better still with diphenylphosphinebutylsulphonate DPBS, in conjunction with *N*-methylpyrrolidone as a solubilizer. This produces a homogeneous mixture that can be easily split into two phases by addition of water or methanol at the end of the reaction [1,5]. Aqueous biphasic technologies are generally considered very "green", as they avoid the use of large amounts of polluting volatile organic solvents.

A different set of very interesting new applications of hydroformylation chemistry involves the treatment of mixtures of valuable medium-chain alkenes -mainly in the C4–C7 range- present in refinery cuts and sometimes referred to as "orphan olefins", for which there are few commercial uses. Examples of such applications have been reported e.g. for the conversion of raffinate-2 (but-1-ene + but-2-ene) [1,2] and also for the production of high-performance plasticizers like di-iso-nonylphtalate [6]. Along these lines, we are interested in the fact that refinery naphtha (the basis for gasoline) contains up to 50% vol. of C5–C7 alkenes of varied structures, while specifications for the final product allow no more than about 12%. Currently, the excess of olefins in naphtha is lowered by hydrogenation over standard solid catalysts, which is costly and results in a marked decrease in the octane rating of the fuel. This is subsequently corrected by addition of methylterbutylether (MTBE) but this gasoline additive is highly polluting because of its water solubility and it is therefore being rapidly phased out, while less harmful oxygenated components are expected to replace it in the near future. Hydroformylation could thus be an interesting novel method for lowering the olefin content of naphtha through the in situ conversion of some of the alkenes present into valuable C5–C8 oxygenates (aldehydes or alcohols), capable of improving the combustion properties of the fuel while at the same time being less water-soluble and less harmful than MTBE. For this type of application, the regioselectivity of the catalysts (*n*/*i* ratios) is unimportant, since both linear and branched aldehydes or alcohols would be acceptable in the final product, thus resulting in an extremely favorable atom economy with virtually no waste.

In view of the large volumes of refinery cuts that need to be treated, a classical homogeneous system requiring costly or complicated product separation from the catalyst would not be practical and therefore we have turned our attention to liquid biphasic systems (aqueous and ionic liquids). We have recently reported the use of Ru(II) catalysts containing TPPMS in the aqueous-biphasic hydroformylation of alkene mixtures as models of naphtha components [7]. In the present paper we describe a comparative study of the Rh-catalyzed hydroformylation of C6 alkenes and alkene mixtures in homogeneous and aqueous-biphasic media using PPh_3, TPPTS, and TPPMS ligands, as a further demonstration of the considerable potential of these "green" systems for applications related to fuel upgrading issues.

2. Experimental

2.1. General procedure

All manipulations were carried out under nitrogen using standard Schlenck techniques. Organic solvents and olefins were dried and purified by distillation over standard agents under N_2 prior to use. $RhCl_3 \cdot 3H_2O$ was purchased from Pressure Chemicals and alkenes were obtained from Aldrich and distilled from Na under nitrogen or argon. All other chemicals were commercial products and were used without further purification. All gases were of high purity (>99%) and were purchased from AGA Gases. $RhH(CO)(PPh_3)_3$ [8], TPPTS, TPPMS [9], $RhH(CO)(TPPTS)_3$, and $RhH(CO)(TPPMS)_3$ [10] were synthesized according to published methods. Infrared spectra were recorded in Perkin–Elmer 1000 or Nicolet Magna 560 FTIR spectrometers using pressed samples as KBr disks. GC analyses were performed on a Hewlett Packard 5890 Plus Series II chromatograph with a flame ionization detector and ultra 2.5% phenyl methyl silicone, 25m, 320 μm column. Quantification was achieved by using naphthalene as the internal standard and all peaks were identified by GC/MS on a HP 5890/5972 coupled system using a Quadrex PONA 5% phenyl methyl silicone, 25 m, 320 μm column.

2.2. Catalytic hydroformylation

All the catalytic reactions were performed under constant pressure in glass-lined stainless steel autoclaves (Parr) fitted with internal mechanical stirring, a high-pressure reservoir, temperature control unit, and a sampling valve. For each catalyst, a hydroformylation run was carried out in the presence of excess mercury

(1 ml, 7×10^{-2} mol) for HX1E and for the four-component mixture, in order to ascertain the possible involvement of metallic particles or colloids in the catalysis [11].

2.2.1. Homogeneous reactions

Typically the catalyst (10 mg, 10^{-5} mol), the alkene (0.5 ml, 4.0×10^{-3} mol), and the solvent (40 ml) were introduced into the reactor. The system was purged three times with CO/H_2 (1:1, 5 atm), charged to the desired pressure and heated to the chosen reaction temperature with constant stirring at 600 rpm (the time required to attain thermal equilibrium was ca. 1 h, during which some hydroformylation ($\leqslant$10% conv.) was observed). Samples were periodically withdrawn for analysis and at the end of the run the reactor was cooled in ice and vented before opening it for the analysis of the final reaction mixture.

2.2.2. Biphasic reactions

In a typical experiment, an aqueous solution of the catalyst precursor (10^{-5} mol) in 20 ml of water and the alkene or alkene-mixture (6×10^{-3} mol) in 20 ml of *n*-heptane were introduced into the reactor. The solution was purged three times with CO/H_2 (1:1, 5 atm), then it was charged to the required pressure, heated to the desired temperature and stirring at 600 rpm was commenced, which defines the zero time of the reactions. Samples of the reaction mixture were periodically extracted and the total pressure was adjusted via a high pressure reservoir. The samples were cooled, the phases separated and the organic phase analyzed by GC-MS. At the end of the run, the reactor was cooled in ice and vented before opening it for analysis of the final reaction mixture. In the anaerobic recycling experiments, after the end of each run the reactor was cooled to room-temperature, the olefin was injected into the reactor by means of a high-pressure burette, the pressure was adjusted to the required value and stirring was re-started immediately to initiate a new run.

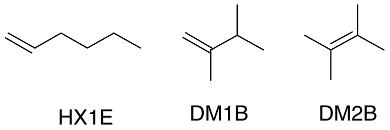


Chart 1.

3. Results and discussion

3.1. Homogeneous hydroformylation of C6 alkenes and alkene mixtures by use of $RhH(CO)(PPh_3)_3$

In order to establish a basis for comparison for the aqueous biphasic systems of particular interest here, we have carried out a series of experiments in the hydroformylation of hex-1-ene (HX1E), 2,3-dimethylbut-1-ene (DM1B), and 2,3-dimethylbut-2-ene (DM2B), which are representative of C6 mono-, di- and tetra-substituted alkenes present in naphtha (Chart 1). HX1E has been employed numerous times in hydroformylation studies but the more hindered terminal alkene DM1B and its tetra-substituted internal isomer DM2B have been less frequently used in this reaction [1,2].

Fig. 1(a) shows the behavior of $RhH(CO)(PPh_3)_3$ in the hydroformylation of HX1E. The apparent induction period observed during the first hour of reaction corresponds to the time required to attain thermal equilibration and in part also to form the active species $RhH(CO)_n(PPh_3)_m$(alkene) in appreciable concentrations. Under the moderate reaction conditions chosen as our standard (60 °C, 15 atm CO/H_2) the reaction proceeds at reasonable rates to produce the two corresponding isomeric aldehydes, *n*-heptanal and 2-methylhexanal in a 3:1 ratio, as typically found for this catalyst in the absence of excess phosphine. No isomerization or hydrogenation products were detected under these conditions.

On raising the reaction conditions to 100 °C and 20 atm H_2/CO the hydroformylation of HX1E is achieved with a rate slightly over twice that observed at the lower

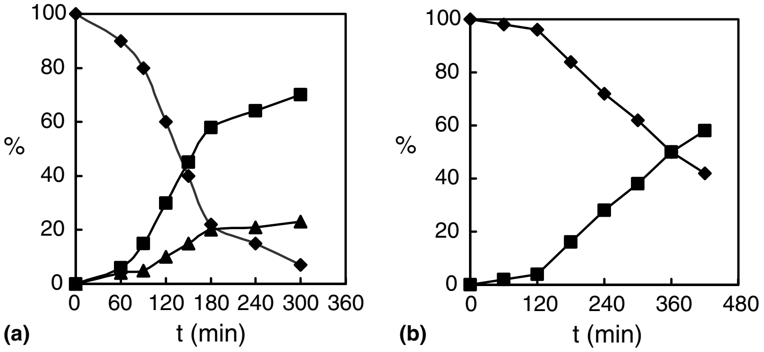


Fig. 1. Hydroformylation by $RhH(CO)(PPh_3)_3$ in toluene. 60 °C, 15 atm CO/H_2 (1:1), [olefin]:[Rh] = 400. (a) (◆) Hex-1-ene; (■) 1-heptanal; (▲) 2-Me-hexanal. (b) (◆) 2,3-Dimethyl-1-butene; (■) 3,4-dimethylpentanal.

conditions employed. When DM1B is hydroformylated under the milder conditions (60 °C, 15 atm CO/H_2), the reaction profile shown in Fig. 1(b) is observed. In this case, the induction period is of about 2h, indicating that even after reaching the thermal equilibrium, the reaction is very slow for another hour, after which a linear behavior up to ca. 60% conversion is observed, albeit at a lower rate than the one observed for HX1E. This implies that the formation of the active species in sufficient concentration is slower for the more hindered alkene. As expected, the sole reaction product is 3,4-dimethylpentanal, the "linear" isomer of the hydroformylation; it is known that the "branched" product is not formed in this case because of the strong steric congestion that would be caused by two methyl groups in the vicinity of the rhodium center in the corresponding alkyl intermediate. Similarly to what was observed for HX1E, no isomerization or hydrogenation products were detected under the conditions employed. The turnover frequencies (TOF) of these two reactions were calculated from the slopes of the linear portion of each plot in Fig. 1, and the corresponding values are collected in Table 1.

When the tetra-substituted alkene DM2B was subjected to hydroformylation under analogous conditions, only 4% conversion was observed after 24h reaction and the only product detected was 3,4-dimethylpentanal, again the "linear" isomer of the hydroformylation of DM1B. This indicates that the catalysts is capable of slowly isomerizing DM2B to DM1B under the conditions employed and hydroformylation occurs only when the C═C bond of the former has shifted to the terminal position. In this case the TOF was estimated from the percentage conversion after 24 h and the corresponding value is included in Table 1. From these data it can be deduced that the rate of hydroformylation of HX1E is about three times faster than that of DM1B and about 250 times faster than the rate of isomerization–hydroformylation of DM2B. On raising the temperature to 120 °C and the pressure to 68 atm, the isomerization–hydroformylation of the very un-reactive tetra-substituted olefin can be achieved with conversions of about 50% in 5h, corresponding to a reasonable TOF of ca. 0.8 min^{-1}.

When a 1:1:1 mixture of the three alkenes was hydroformylated under our standard conditions for 5 h, the conversion of HX1E dominated the reaction, while the relative activity for the conversion of DM1B was lowered in comparison with the case of the pure olefins by about 30%, and DM2B did not react. This indicates that there is a competition for the active Rh sites in favor of the coordination of the less hindered alkene HX1E, and the result of that is that the hydroformylation of DM1B becomes significant only when more than 50% of HX1E has been consumed. For practical purposes concerning possible naphtha upgrading applications, it was interesting to evaluate this catalyst in the hydroformylation of the three-component mixture, under the more stringent conditions necessary to effect the conversion of the least reactive, most hindered alkene DM2B (120 °C, 68 atm CO/H_2). As can be seen in Fig. 2, no induction period is present in this case, as a much faster heating rate can be employed to stabilize our reactor at 120 °C. Also, it is noted that the three substrates react in a consecutive manner: HX1E is completely consumed within the first 30 min in this case. The formation of 3,4-dimethylpentenal starts when most of the HX1E has been converted and it is fairly rapid at the early stages of the reaction but after 50% conversion a slower reaction rate is observed. These two kinetic regimes correspond to the

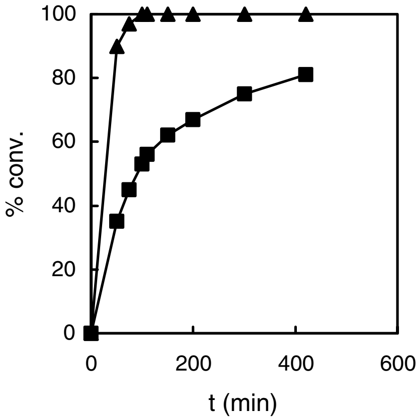


Fig. 2. Hydroformylation of a 1:1:1 mixture of HX-1E, 2,3-DM1B, 2,3-DM2B by $RhH(CO)(PPh_3)_3$ in toluene. 120 °C, 68 atm CO/H_2 (1:1), $[\text{olefin}]_{\text{tot}}$:[Rh] = 400. (a) (▲) *n*-Heptanal + 2-Me-hexanal; (■) 3,4-dimethylpentanal.

Table 1
Hydroformylation of alkenes by $RhH(CO)(PPh_3)_3$ (conditions: H_2/CO (1:1), [alkene]:[Rh] = 400)

Alkene	*T* (°C)	*P* (atm)	*t* (h)	% conv.	TOF (min^{-1})[a]	Rel. Act.
HX1E	100	20	0.75	56	5.0	–
HX1E	60	15	2	50	2.3	1.0
DM1B	60	15	6	50	0.75	0.3
DM2B	60	15	24	4	0.01[b]	0.004
DM2B	120	68	5	50	0.8[b]	–

[a] Values calculated from the maximum slopes in the plots shown in Fig. 1.

[b] Average values estimated from (% conversion/*t*).

direct hydroformylation of DM1B (faster), followed by the slower isomerization–hydroformylation of DM2B.

A last point of interest concerning reactions of refinery cuts is that they usually contain small amounts of organo-sulfur compounds that may act as poisons toward the catalyst. In order to model such a situation, the hydroformylation of a mixture containing the three alkenes plus thiophene or benzothiophene in a 1:1:1:1 molar ratio was carried out under analogous conditions to the ones reported in Fig. 2 (120 °C, 68 atm CO/H_2 (1:1), $[\text{olefin}]_{\text{tot}}$:[Rh] = 400). No inhibition of the hydroformylation reaction was observed, but instead a slight increase in the overall conversion could be measured (about 10% for thiophene and about 20% for benzothiophene). Sulfur tolerance has been previously recognized for Rh-phosphine catalysts [2] but it is important to note that in our experiments $RhH(CO)(PPh_3)_3$ was not only resistant to poisoning by organosulfur compounds at concentrations much higher than the ones normally expected to be present in a naphtha, but a *promotion* effect was actually observed. This point will be the object of future studies.

3.2. Aqueous biphasic hydroformylation of C6 alkenes and alkene mixtures by use of $RhH(CO)(TPPTS)_3$

Under reaction conditions analogous to the ones selected for the homogeneous reactions, the complex $RhH(CO)(TPPTS)_3$ is not a good catalyst for the two-phase hydroformylation of HX1E in water/*n*-heptane mixtures. The reaction is very slow at temperatures of 60 °C or below but reasonable rates are achieved at 80 °C or above. However, at low pressures of syngas (<30 atm) HX1E is rapidly converted mainly to hex-2-ene (ca. 60–70%) while the production of aldehydes is only observed as a minor reaction. Nevertheless, at pressures between 50 and 68 atm isomerization is strongly disfavored (<20% of the total conversion) and hydroformylation dominates. A typical reaction profile under optimized conditions is shown in Fig. 3(a), indicating that isomerization competes with hydroformylation at the early stages of the reaction but after about 30 min the production of aldehydes prevails. Representative data indicating the total aldehyde production (linear + branched) with this aqueous system as a function of temperature and pressure are shown in Fig. 3(b). Thus, by adequately adjusting the operation parameters, the biphasic system can be tuned to efficiently promote alkene hydroformylation.

These observations are in contrast with the behavior of the homogeneous system $RhH(CO)(PPh_3)_3$, which does not promote C=C bond isomerization. However, they are consistent with the low solubility of hex-1-ene and of syngas in water. At low pressures, the olefin can come into contact with the catalyst, either in the water phase or possibly in the liquid–liquid interface, but the concentration of syngas in that region is very low. Consequently, a classical metal-hydride promoted C=C bond migration mechanism becomes dominant and most of the terminal alkene is converted rapidly to the internal isomer that is more resistant to hydroformylation. As the gas pressure is increased the effective concentration of CO and H_2 at the catalytic site is sufficient for hydroformylation to be faster than isomerization. From the data in Fig. 3(b), optimum hydroformylation conditions are chosen as 80 °C and 55 atm CO/H_2, under which the isomerization side-reaction is almost completely suppressed and ca. 100% conversion to aldehydes is achieved in 2.5 h. The *n*/*i* ratios in the experiments at 80 °C or 100 °C were systematically of the order of 1.5, where 2-Me-hexanal originates from both hex-1-ene and the small amounts of hex-2-ene formed. Also, a small proportion (<10%) of 2-Et-pentanal, the other product of hex-2-ene hydroformylation, was consistently detected. Addition of free TPPTS in concentrations up to 8 moles per mol of complex did not result in a significant variation of the selectivity. This indicates that under the relatively high CO pressures required to obtain reasonable rates and a good chemoselectivity of hydroformylation in the biphasic

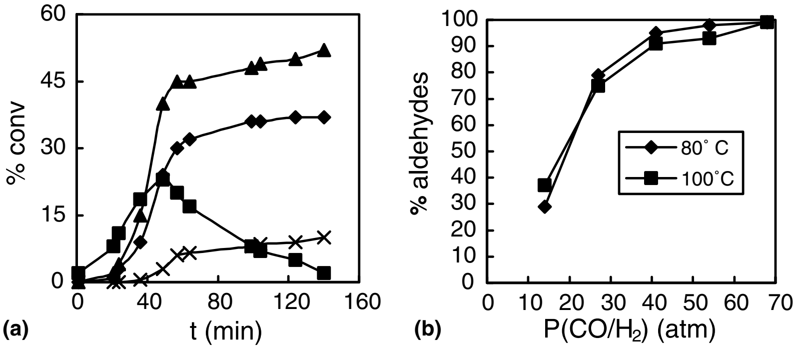
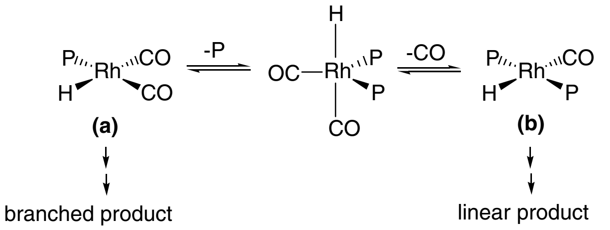


Fig. 3. Biphasic hydroformylation of hex-1-ene in H_2O/*n*-heptane by use of $RhH(CO)(TPPTS)_3$. (a) Reaction profile at 80 °C, 55 atm CO/H_2, [olefin]:[Rh] = 600; (■) hex-2-ene; (▲) 1-heptanal; (◆) 2-Me-hexanal; (×) 2-Et-pentanal. (b) Effect of *T* and *P* on the total production of aldehydes after 2.5 h.

system, the monophosphine species **a**, which is the least regioselective intermediate, predominates in the equilibrium shown in Scheme 1 and addition of free-phosphine does not shift this equilibrium to an important degree toward the more sterically hindered bis(phosphine) intermediate **b** that would be more selective for the production of linear products.

In agreement with this, the IR spectra of samples withdrawn under a syngas stream from the thermally equilibrated catalytic solutions at the working pressure, with or without excess TPPTS but in the absence of the olefin, were dominated by features corresponding to a *dicarbonyl* species, possibly **a** (ν_{CO} 2000, 2020 cm^{-1}; ν_{Rh-H} 2052 cm^{-1}). This behavior is again in contrast with the homogeneous system, which does not require very high pressures to operate with reasonable rates and is known to produce very high *n*/*i* ratios in the presence of excess PPh_3 via bis(phosphine)intermediates like **b**. Attempts to carry out the analysis of such mixtures by ^{31}P NMR spectroscopy failed, because the samples decomposed during the time required for their manipulation from the high-pressure reactor into the NMR tube, even under a syngas stream.



Scheme 1.

In view of the good performance of the aqueous catalyst for hex-1-ene hydroformylation, and of the results obtained for other alkenes with the analogous homogeneous system, it was decided to further evaluate the catalytic properties of $RhH(CO)(TPPTS)_3$ for the hydroformylation of DM1B, styrene (STY) and cyclohexene (CHX), which better represent the components of a refinery cut. DM2B was no longer considered in this part of the study, because of its highly un-reactive nature and due to the fact that real refinery naphtha contains only very small amounts of tetra-substituted olefins [12]. Fig. 4 depicts typical reaction profiles for these three alkenes.

Under the reaction conditions optimized for HX1E (80 °C, 55 atm CO/H_2, [substrate]:[Rh] = 600) DM1B is hydroformylated with reasonable rates, achieving 100% conversion after about 3 h with a short induction period (<30 min) (Fig. 4(a)). Styrene is also hydroformylated efficiently (100% conv. in less than 5 h) to the two corresponding aldehydes (Fig. 4(b)) with a selectivity for

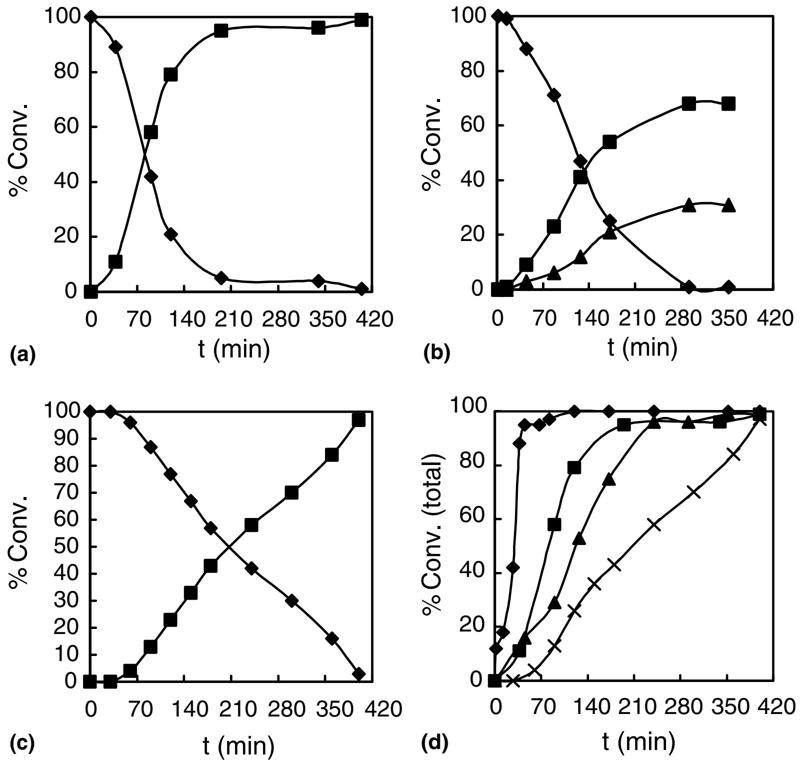


Fig. 4. Biphasic hydroformylation by $RhH(CO)(TPPTS)_3$ in H_2O/*n*-heptane; 80 °C, 55 atm CO/H_2, [subst.]:[Rh] = 600. (a) (◆) 2,3-Dimethyl-1-butene; (■) 3,4-dimethylpentanal. (b) (◆) Styrene; (■) 2-phenyl-propanal; (▲) 3-phenyl-propanal. (c) (◆) Cyclohexene; (■) cyclohexanecarboxaldehyde. (d) Total conversions for (◆) hex-1-ene; (■) 2,3-dimethyl-1-butene; (▲) styrene; (×) cyclohexene.

the branched isomer typical of this reaction at temperatures around 100 °C (*n*/*i* ca. 0.3 at <50% conversion and about 0.5 at high conversions) [1]. Cyclohexene, as expected, was the least reactive of the alkenes studies, reaching 100% conversion after about 7 h and displaying an induction period of ca. 30 min, presumably reflecting the slower formation of $RhH(CO)_n(TPPTS)_n(CHX)$ in appreciable concentrations (Fig. 4(c)). For comparison, Fig. 4(d) shows the total conversions for each alkene as a function of time. Plots of the linear section of each curve (in turnover number units, TON) allowed us to calculate the TOF values collected in Table 2.

From these data it is seen that the hydroformylation of HX1E is about three times faster than that of DM1B, four times faster than that of STY and 7.5 faster than that of CHX. All the alkenes tested can thus be efficiently converted to aldehydes by $RhH(CO)(TPPTS)_3$ in a biphasic mixture under moderate reaction conditions. Only HX1E produced small amounts of isomerization by-products, thus making this a promising system for naphtha upgrading applications.

Table 2
Aqueous biphasic hydroformylation of alkenes by $RhH(CO)(TPPTS)_3$ (conditions: 80 °C, 54 atm H_2/CO (1:1), [alkene]:[Rh] = 600)

Alkene	*t* (h)	% conv.	TOF (min^{-1})[a]	Rel. Act.
HX1E	1.5	100	13.5	1.0
DM1B	3	100	5.0	0.4
STY	4.5	100	3.4	0.25
CHX	7	100	1.8	0.13

[a] Values calculated from the maximum slopes of the plots in Fig. 4.

When a 1:1:1:1 mixture of the four olefins was hydroformylated, the results displayed in Fig. 5(a) were obtained. It is clear from these data that in the mixture, the reactions are consecutive and not parallel, and under these conditions STY is converted more rapidly than DM1B, in contrast to what is observed for the individual substrates. Cyclohexene only reacts appreciably after about 7 h, when most of the other alkenes have been consumed. These observations indicate that when several olefins are present simultaneously, a competition for the metal centers takes place leading to a reactivity order in this case HX1E > STY > DM1B > CHX. The inversion in the relative reactivity of STY and DM1B observed in the mixture with respect to the individual components probably results from a combination of the differences in their water-solubility and in their intrinsic strengths of coordination to Rh.

The reaction profile in terms of total olefin conversion depicted in Fig. 5(b) also shows the trend of a rapid initial period (up to about 90 min) with no induction period, corresponding to the complete hydroformylation of HX1E plus the partial conversion of the two other terminal olefins, after which a slower regime is observed essentially for the hydroformylation of STY and DM1B, while the reaction of CHX contributes little to the overall conversion. Addition of 50 ppm of benzothiophene did

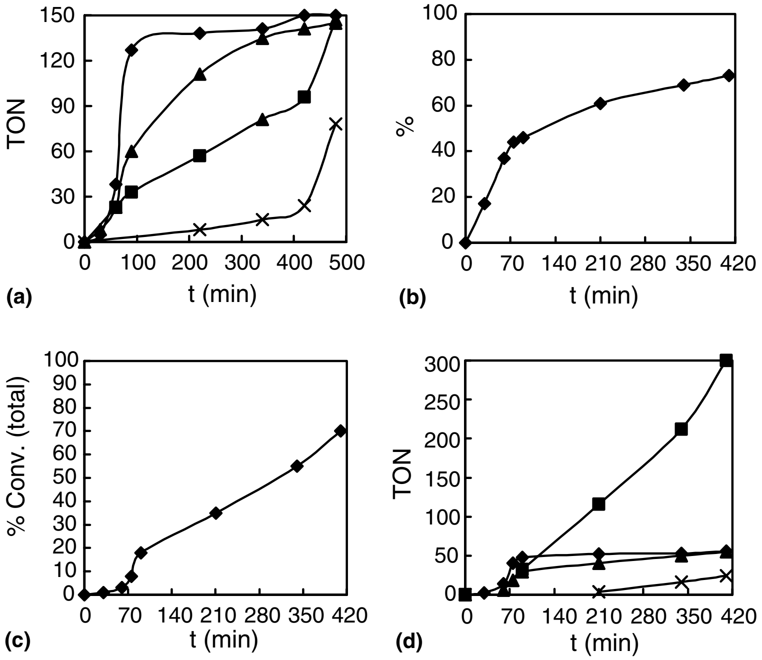


Fig. 5. Hydroformylation of mixtures of hex-1-ene, styrene, 2,3-dimethyl-1-butene and cyclohexene by $RhH(CO)(TPPTS)_3$ in H_2O/*n*-heptane at 80 °C, 55 atm CO/H_2, $[olefin]_{tot}$:[Rh] = 600. For a 1:1:1:1 molar ratio: (a) TON values: (◆) hex-1-ene; (▲) styrene; (■) 2,3-dimethyl-1-butene; (×) cyclohexene. (b) Total olefin % conversion. For a HX1E : STY: CHX : DM1B molar ratio of 1:1:1.5:7: (c) Total olefin % conversion. (d) TON values: (◆) hex-1-ene; (■) 2,3-dimethyl-1-butene; (▲) styrene; (×) cyclohexene.

not have any effect on the catalyst behavior under the conditions of Fig. 5(b).

Finally, another mixture of the four olefins was prepared containing the proportions HX1E:STY:CHX:DM1B = 1:1:1.5:7, which are analogous to those found in a real naphtha for mono-substituted, cyclic, and di-substituted alkenes [12]. The results of the hydroformylation of such a naphtha-model mixture at 80 °C, 55 atm CO/H_2, [total olefins]:[Rh] = 600 are depicted in Fig. 5(c). It is clearly noted that after an induction period of about 1h, a first rapid hydroformylation regime operates up to about 20% conversion, followed by a slower reaction reaching a total conversion of ca. 70% after 7 h. TON values for each individual olefin are also presented in Fig. 5(d), showing again a behavior of the whole mixture corresponding to a set of consecutive reactions that correlate well with the initial composition of the mixture.

The terminal olefins (HX1E + DM1B + STY) are all hydroformylated with reasonably fast rates that are comparable to each other. Their combined conversion corresponds to the faster regime in Fig. 5(a). Once

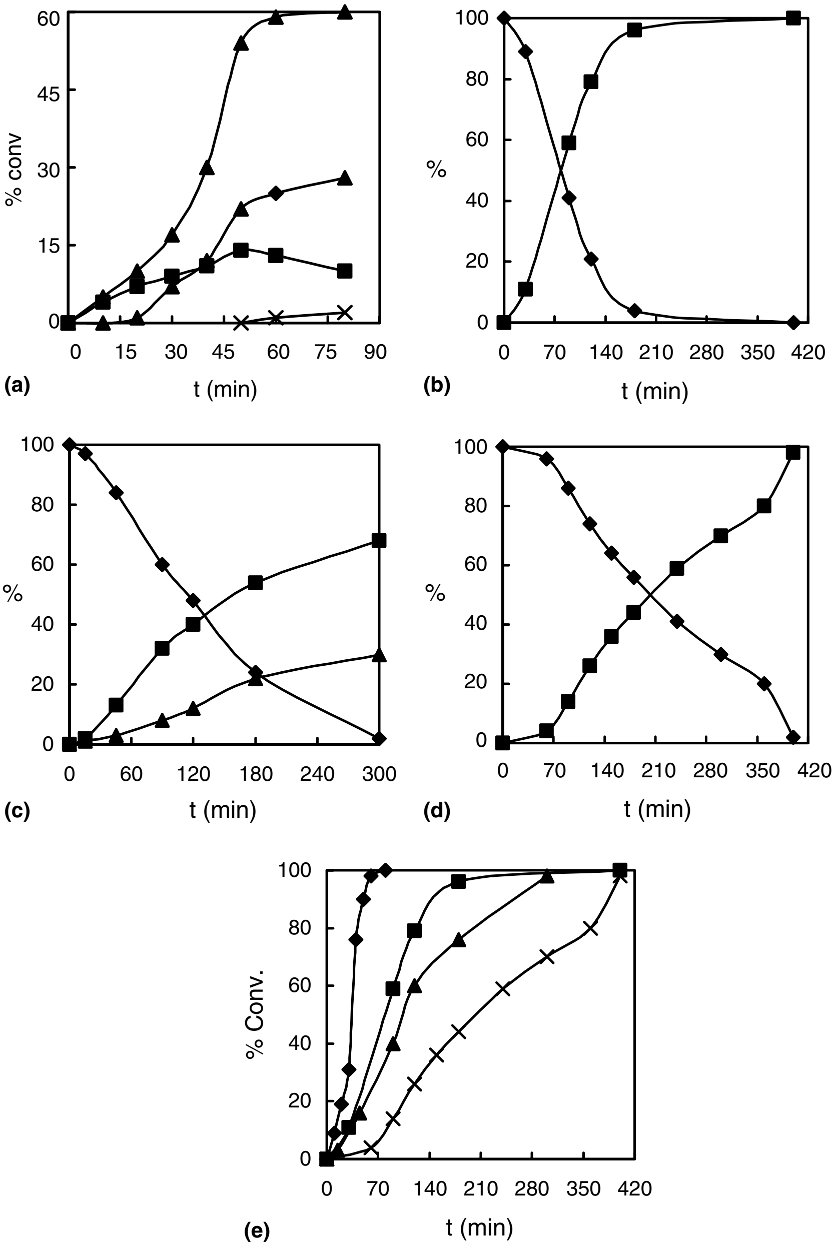


Fig. 6. Hydroformylation by RhH(CO)(TPPMS)$_3$ in H_2O/*n*-heptane; 80 °C, 55 atm CO/H_2, [subst.]:[Rh] = 600. (a) (■) Hex-2-ene; (▲) 1-heptanal; (◆) 2-Me-hexanal; (×) 2-Et-pentanal. (b) (◆) 2,3-Dimethyl-1-butene; (■) 3,4-dimethylpentanal. (c) (◆) Styrene; (■) 2-phenyl-propanal; (▲) 3-phenyl-propanal. (d) (◆) Cyclohexene; (■) cyclohexanecarboxaldehyde. (e) Total conversions for (◆) hex-1-ene; (■) 2,3-dimethyl-1-butene; (▲) styrene; (×) cyclohexene.

HX1E and STY (amounting to about 20% of the mixture) have been totally consumed, hydroformylation of DM1B takes place almost exclusively, which represents an overall lower rate accounting for the change in slope observed in Fig. 5(a). CHX only begins to react after 3.5 h, when an important proportion of DM1B has been converted. At the end of the 7 h run, the final composition shows that HX1E and STY have been completely transformed into aldehydes, DM1B has been converted in ca. 75% and CHX in about 30%. The general trend in reactivity observed for the equimolar mixture of olefins is maintained in this case, but concentration effects obviously also come into play. The importance of the latter experiment is to demonstrate the practical potential of the biphasic system, which can reduce the overall olefin content in a naphtha-model mixture by 70% in 7 h, converting the unsaturated compounds almost exclusively into oxygenates.

3.3. Aqueous biphasic hydroformylation of C6 alkenes and alkene mixtures by use of RhH(CO)(TPPMS)$_3$

Because of its extreme water-solubility the TPPTS-derived catalyst is only used industrially for the hydroformylation of short-chain alkenes that are moderately soluble in water; the reaction in those cases is thought to occur predominantly in the aqueous phase [1–4]. Longer-chain alkenes like the ones used in the present study are very sparingly soluble in water and therefore their reactions take place preferentially in the organic phase or at the liquid–liquid interface. The TPPMS complex RhH(CO)(TPPMS)$_3$, being less soluble in water than the trisulfonated analogue, is probably a better suited catalyst for the hydroformylation of C6 alkenes, since its concentration at the liquid–liquid interface is higher and it actually has surfactant properties [13].

As shown in Fig. 6, this catalyst is also efficient for the hydroformylation of HX1E, DM1B, STY and CHX in water/*n*-heptane mixtures under reaction conditions similar to the ones used for the TPPTS derivative (80 °C, 55 atm CO/H$_2$, [substrate]:[Rh] = 600). From the linear sections of the plots in Fig. 6(e), the TOF values collected in Table 3 could be calculated. It is observed that these values are similar to those obtained for the TPPTS catalyst, and both of them are comparable with homogeneous systems except that low pressures cannot be employed in biphasic conditions due to gas solubility limitations.

Table 3
Aqueous biphasic hydroformylation of alkenes by RhH(CO)(TPPMS)$_3$ (conditions: 80 °C, 54 atm H$_2$/CO (1:1), [alkene]:[Rh] = 600)

Alkene	*t* (h)	% conv.	TOF (min^{-1})[a]	Rel. Act.
HX1E	1	100	14.1	1.0
DM1B	3	100	4.4	0.3
STY	5	100	2.9	0.2
CHX	7	100	2.0	0.14

[a] Values calculated from the maximum slopes of the plots in Fig. 6.

For an equimolar mixture of the four alkenes, the behavior of the TPPMS catalyst is also similar to that of the TPPTS analogue (Fig. 7). HX1E reacts much faster than the other alkenes, STY is more rapidly converted than DM1B and CHX only starts to react at long reaction times, when most of the other substrates have been consumed. Addition of 50 ppm of benzothiophene had no influence on the hydroformylation of the four-component alkene mixture under the conditions of Fig. 7.

3.4. Re-using the aqueous biphasic hydroformylation catalysts

One of the main reasons for using aqueous biphasic catalysts is the possibility of easily separating them from the products at the end of the reaction and re-using them. In order to test the recycling capacity of our catalysts, a first series of experiments were carried out with HX1E as the substrate and RhH(CO)(TTPMS)$_3$ as the catalyst precursor: the reactor was opened under a stream of nitrogen at the end of a catalytic run (80 °C, 55 atm CO/H$_2$, [HX1E]:[Rh] = 600, 2 h), the organic phase was syringed out, a new charge of fresh substrate in *n*-heptane was added, and the reactor was re-sealed, pressurized and heated for a new hydroformylation run. In four consecutive cycles performed in this way with the same catalyst solution, the conversion values were 100%, 100%, 100% and 80%. The lowering in the catalyst activity observed after the fourth cycle can be attributed to decomposition of the catalyst solution by contact with air. Indeed, more satisfactory results were obtained by use of an alternative procedure: a similar reaction was performed to 100% HX1E conversion; the reactor was then cooled to room-temperature but not opened, a new charge of substrate was introduced through a high-pressure burette, and a new catalytic run was performed; in this case the conversion of HX1E was consistently greater than 97% in four consecutive cycles, for both the TPPMS and the TPPTS catalysts.

3.5. Stability of the aqueous biphasic hydroformylation catalysts

It is known that both the active species and the excess ligand of the Rh-TPPTS system in industrial use are subject to slow decomposition, requiring repeated addition of fresh ligand to maintain the [Rh]:[P] ratio and of sulfuric acid to avoid large variations of the pH of the solution. If these precautions are not taken, faster hydroformylation rates may be observed after some time due to changes in the composition of the catalyst or to

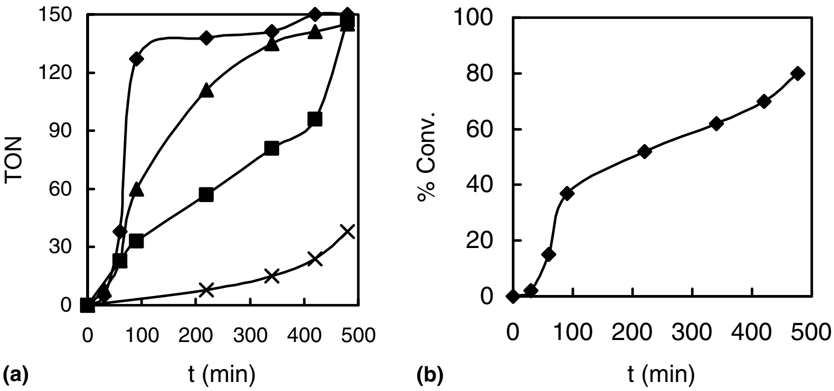


Fig. 7. Hydroformylation of a HX1E : STY: CHX : DM1B 1:1:1:1 mixture by RhH(CO)(TPPMS)$_3$ in H_2O/*n*-heptane; 80 °C, 55 atm CO/H_2, [subst.]:[Rh] = 600. (a) Total aldehyde production for (◆) hex-1-ene; (▲) styrene; (■) 2,3-dimethyl-1-butene; (×) cyclohexene. (b) Total alkene conversion.

the formation of Rh colloids [1–4]. The hydroformylation of HX1E and of the four-component mixtures were carried our in the presence of an excess of mercury under optimized conditions for the two biphasic catalysts (80 °C, 55 atm CO/H_2, [substrate]:[Rh] = 600, [Hg]:[Rh] ca. 7000). In all cases the reaction profile was essentially the same as in the absence of mercury, within experimental error (data not shown), indicating that there is no participation of metallic particles or colloids in the catalysis under our reaction conditions. Analyses of the final mixtures by ^{31}P NMR spectroscopy were not informative because the samples appeared to decompose rapidly after the reactor pressure was released and during their preparation for the spectroscopic measurement. An in situ high-pressure NMR analysis would probably help to clarify this point, but it is in any case unlikely that extensive catalyst decomposition would take place under our moderate conditions during the relatively short reaction times employed in this work.

3.6. Conclusion

The results presented here demonstrate that aqueous biphasic catalysts derived from RhH(CO)L$_3$ (L = TPPTS or TPPMS) can hydroformylate C6 alkenes and alkene mixtures with reasonable rates under moderate reaction conditions. The main problem associated with these catalysts is their strong tendency to isomerize C=C bonds from the terminal to an internal position if the effective syngas concentration at the interface is low, but this side-reaction can be suppressed by using higher but still reasonable pressures around 50 atm. The modest selectivity of this system for the production of linear aldehydes from hex-1-ene or for branched aldehydes from styrene may limit their applicability to classical oxo uses, but this would not be a great disadvantage for other applications involving olefin mixtures, in particular for the important problem of naphtha upgrading, since in this case both linear and branched products would be equally useful. Moreover, the isomerization side-reaction is not necessarily a serious drawback for this type of application, as final gasoline specifications allow up to 12% of olefins and the internal isomers are actually convenient since they provide a much higher octane rating than the terminal ones [2]. The properties of the two biphasic systems reported here did not change significantly when the catalysts were recycled up to four times under anaerobic conditions, and addition of sulfur-containing compound like benzothiophene in concentrations up to 50 ppm did not cause any important inhibition of the catalysis. In this respect, the aqueous biphasic systems constituted by RhH(CO)(TPPTS)$_3$ and RhH(CO)(TPPMS)$_3$ can be considered as promising alternatives for naphtha treatment and related applications. In future papers we will describe similar work using low-temperature ionic liquids as the immobilization media for hydroformylation catalysts.

Acknowledgements

We thank FONACIT (Caracas) for financial support through Project CONIPET 97-003777, CODECIHT-UC (Valencia) through Project 94017, and CYTED (Madrid) through Project V.9.

References

[1] P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium catalyzed hydroformylationB.R. James, P.W.N.M. van Leeuwen (Eds.), Catalysis by Metal Complexes Series, vol. 22, Kluwer Academic Publishers, Dordrecht, 2000.

[2] C.D. Frohning, C.W. Kohlpaintner, H.-W. Bohnen, second ed., in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, Wiley-VCH, Weinheim, 2002, pp. 31–103 (Chapter 2.2.1).

[3] B. Cornils, W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, second ed., Wiley-VCH, Weinheim, 2002, pp. 603–633 (Chapter 3.1.1.1).

[4] B. Cornils, W.A. Herrmann (Eds.), Aqueous-phase Organometallic Catalysis. Concepts and Applications, Wiley-VCH, Weinheim, 1998;
C.W. Kohkpaintner, R.W. Fischer, B. Cornils, Appl. Catal. A: General 221 (2001) 219.

[5] A.G. Abatjoglou, D.R. Bryant, U.S. Pat. (to Union Carbide) 4,731,486 (1988); A.G. Abatjoglou, 209th ACS Natnl. Meeting (1995); Chem. Eng. News 1995, April 17th, p. 25.

[6] D. He, D. Pang, T. Wang, Y. Chen, Y. Liu, J. Liu, Q. Zhu, J. Mol. Catal. 174 (2001) 21.

[7] P.J. Baricelli, E. Lujano, M. Rodríguez, A. Fuentes, R.A. Sánchez-Delgado, Appl. Catal. A: General 263 (2004) 187.

[8] N. Ahmad, J.J. Levinson, S.D. Robinson, M.F. Uttley, Inorg. Synth. 28 (1990) 82.

[9] F. Joó, J. Kovács, A. Kathó, A. Bényei, A.C. Decuir, D.J. Darensbourg, Inorg. Synth. 32 (1998) 2.

[10] A.F. Borowski, D.J. Cole-Hamilton, G. Wilkinson, Nouv. J. Chim. 2 (1978) 137.

[11] (a) R.H. Crabtree, Organometallics 1 (1983) 855;
(b) J.A. Widegreen, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317.

[12] Technical Report from ‘‘El Palito’’ Refinery, PDVSA, Venezuela.

[13] (a) A. Andriollo, A. Bolivar, F.A. López, D.E. Páez, Inorg. Chim. Acta 238 (1995) 187;
(b) R.A. Sánchez-Delgado, M. Medina, F. López-Linares, A. Fuentes, J. Mol. Catal. 116 (1997) 167;
(c) A. Andriollo, J. Carrasquel, J. Mariño, F.A. López, D.E. Páez, I. Rojas, N. Valencia, J. Mol. Catal. 116 (1997) 157.