

# Hydroformylation of functionalized olefins catalyzed by water-soluble rhodium carbonyl complexes

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## Abstract

The hydroformylation of 1,1-diarylethenes, 1,1-diaryllallylcohols, and aryl vinyl ethers was carried out in biphasic system water/toluene (cyclohexane) in the presence of rhodium carbonyl complexes with the water-soluble ligand, sulfonated triphenylphosphine  $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3^-\text{Na}^+)_3$  (TPPTS), under standard reaction conditions. The yields of the expected aldehydes are generally high without any addition of co-solvents, hydrophobic auxiliary ligands, or other agents able to improve the transport across the two phases. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydroformylation; Biphasic catalysis ; Rhodium

## 1. Introduction

The crucial advantages of aqueous two-phase hydroformylation reaction, namely, the easy separation of the catalyst from water immiscible products, and the environmental benefits connected with the use of water as the solvent, stimulated a great deal of research work in this field in the last decade [1–6]. Current applications of water-soluble catalytically active rhodium complexes seem to be limited to substrates which exhibit significant water solubil-

ity. Therefore, the only large-scale industrial application of this methodology is the Ruhrchemie Rhône-Poulenc process, in which propene is converted with high chemo- and regioselectivity to *n*-butanal using a rhodium complex of the sulfonated triphenylphosphine,  $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3^-\text{Na}^+)_3$  (TPPTS) as catalytic precursor [7,8]. Usually, reaction rates are low in a two-phase system with higher olefins as the substrates [9,10]. Several approaches have been taken to increase the reaction rate of less water-soluble olefins in the presence of hydrosoluble hydroformylation catalysts; they include: (i) the replacement of the sodium ion in TPPTS or related ligands by a quaternary ammonium cation [11], in order to perform the catalytic process in a polar solvent as, for instance, methanol; (ii) the addition of surfactants to two-phase reaction mixtures [12]; (iii) the use of

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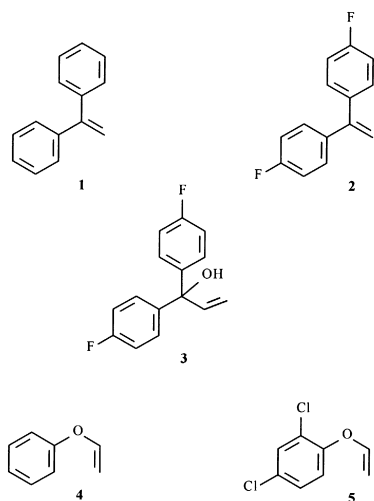


Fig. 1.

surface-active phosphines (amphiphilic ligands), which enable very likely their rhodium complexes to form micelles [9,13]; (iv) the use of agents able to improve the transport rate across the two phases such as hydrophobic auxiliary ligands [14], co-solvents [15], modified cyclodextrins [16], and functionalized polymers [17,18].

This remarkable amount of research work was almost exclusively addressed to the hydroformylation of hydrocarbon olefins; only few and scattered experiments, which employ unconventional olefinic substrates such as olefins containing various functional groups, are reported [17–22].

In our ongoing research work, directed to the preparation of aldehydes and their derivatives to be used as intermediates for the synthesis of different biologically active compounds [23], we have investigated the *oxo*-reaction on the olefinic substrates 1,1-diphenylethene (**1**), 1,1-bis(*p*-fluorophenyl)ethene (**2**), 1,1-bis(*p*-fluorophenyl)-prop-2-en-1-ol (**3**), phenylvinylether (**4**) and 2,4-dichlorophenylvinylether (**5**), in biphasic medium (Fig. 1).

Therefore, all these substrates were already hydroformylated by us using traditional reaction conditions, i.e., rhodium carbonyl complexes as

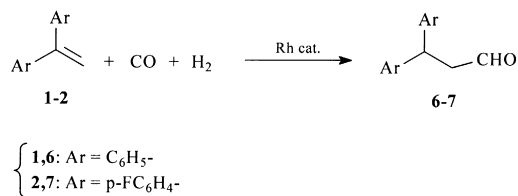
catalytic precursors in hydrocarbon solvents at 80–100 atm ( $\text{CO}/\text{H}_2 = 1$ ) and 60–120°C [23].

In this paper, we report the results obtained in the *oxo*-reaction of **1–5** carried out in water–toluene (or water–cyclohexane) system in the presence of the hydrosoluble catalytic species,  $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$  or  $\text{Rh}(\text{CO})_2(\text{acac})/\text{TPPTS}$ . The use of only TPPTS as water-soluble ligand is based on the fact that this is the only ligand available in large amount at relatively accessible price. A comparison between reaction rate, chemo- and regioselectivity observed in the biphasic process and those in the conventional *oxo*-reaction is made.

## 2. Experimental

### 2.1. General methods and chemicals

Preparative flash chromatography was performed on silica gel if not differently specified. Elemental analyses were performed using an Elemental Analyzer Perkin-Elmer Model 240C. Melting points were determined with a capillary melting point apparatus and are uncorrected. IR spectra were measured with a Bio-Rad Digilab Division model FTS40 as KBr disks or Nujol dispersions as appropriate. Gas chromatographies were recorded with a Perkin-Elmer model 8500 and an HP 5890 gas chromatograph using the appropriate columns and conditions.  $^1\text{H}$  NMR (200 MHz) spectra of  $\text{CDCl}_3$  solutions were recorded using a Bruker AC200 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (300 MHz) spectra of  $\text{CDCl}_3$  solutions were recorded using a Varian VXR 300s spectrometer.



Scheme 1.

Table 1  
Hydroformylation of **1** and of **2** catalyzed by rhodium complexes<sup>a</sup>

Entry	Substrate	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion <sup>b</sup> (%) <sup>b</sup>	Substrate hydrogenation (%)	Aldehyde yield (%)	Aldehyde selectivity <b>6</b> or <b>7</b> (%)
1	<b>1</b>	[RhCl(CO) <sub>2</sub> ] <sub>2</sub>	48	80	75	1	74	> 99
2	<b>1</b>	[RhCl(CO) <sub>2</sub> ] <sub>2</sub> /TPPO	24	100	94	6	88	99
3	<b>1</b>	Rh(CO) <sub>2</sub> (acac)	41	120	86	< 1	85	98
4	<b>1</b>	Rh(CO) <sub>2</sub> (acac) <sup>c</sup>	24	100	99	–	99	> 99
5	<b>2</b>	[RhCl(CO) <sub>2</sub> ] <sub>2</sub> /TPPO	89	100	86	4	82	> 99
6	<b>2</b>	[RhCl(CO) <sub>2</sub> ] <sub>2</sub> /L	15	120	98	10	88	> 99

<sup>a</sup>Substrate 2.3 mmol; toluene 5 ml;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1; Rh/P 1:1 molar ratio.

<sup>b</sup>Determined by GLC analysis.

<sup>c</sup>Catalyst purified by crystallization from *n*-hexane just before the use. TPPO = triphenylphosphite. L = *tris*(2,4-di-*tert*-butylphenyl)phosphite.

Substrate **1**, Rh(CO)<sub>2</sub>(acac), [RhCl(CO)<sub>2</sub>]<sub>2</sub>, Rh<sub>6</sub>(CO)<sub>16</sub>, TPPTS and TPPO were of commercial quality and used as purchased (Aldrich). HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was prepared as described in the literature [24]. Substrates **4** and **5** and *tris*(2,4-di-*tert*-butylphenyl)phosphite were prepared according to literature procedures [25]. 1,1-Bis(*p*-fluorophenyl)ethene [26] and 1,1-bis(*p*-fluorophenyl)prop-2-en-1-ol [27] were prepared as described elsewhere.

## 2.2. General procedure for the hydroformylation of substrates 1–5 in homogeneous phase

A 150-ml stainless steel reaction vessel was charged under nitrogen purge with 5 mmol of the substrate, 0.016 mmol of rhodium catalyst,

0.032 mmol of the ligand of choice if present, and 10 ml of anhydrous toluene. The reactor was then pressurized to 80–100 atm with synthesis gas (CO/H<sub>2</sub> = 1) and heated at 60–120°C for the due time (see tables).

All the aldehydes obtained, **6**, **7** [26,28], hemiacetal (**9**) [27] and **11–14** [25], were purified and characterized as described elsewhere by the authors.

## 2.3. General procedure for the hydroformylation of substrates 1–5 in aqueous biphasic medium

In a Schlenk tube, under nitrogen, 4.0 mg (0.008 mmol) of [Rh(COD)Cl]<sub>2</sub> and 27.6 mg

Table 2  
Hydroformylation of **1** and of **2** in aqueous biphasic medium<sup>a</sup>

Entry	Substrate	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion (%) <sup>b</sup>	Substrate hydrogenation (%)	Aldehyde yield (%)	Aldehyde selectivity <b>6</b> or <b>7</b> (%)
1	<b>1</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	48	100	94	14	80	> 99
2	<b>1</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	70	100	99	14	85	> 99
3	<b>1</b>	Rh(CO) <sub>2</sub> (acac)/TPPTS	48	100	70	4	66	> 99
5	<b>2</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	24	100	59	3	56	> 99
6	<b>2</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	65	100	99 <sup>c</sup>	11	81	> 99
7	<b>2</b>	Rh(CO) <sub>2</sub> (acac)/TPPTS	24	100	59	4	55	> 99
8	<b>2</b>	Rh(CO) <sub>2</sub> (acac)/TPPTS	65	100	88 <sup>d</sup>	11	73	> 99

<sup>a</sup>Substrate 2.8 mmol; solvent = 3.5 ml, H<sub>2</sub>O/toluene = 3:4 v/v;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1; Rh/TPPTS 1:3 molar ratio.

<sup>b</sup>Determined by GLC analysis.

<sup>c</sup>Seven percent high boiling products.

<sup>d</sup>Four percent high boiling products. Hacac = acetylacetonone. TPPTS = triphenylphosphine -3,3',3''-trisulfonic acid trisodium salt.

Table 3  
Conversion and selectivity obtained in the control experiment

Run	Conversion (%)	Substrate hydrogenation (%)	Linear aldehyde (%)
1	69.9	5.0	64.9
2	70.6	5.0	65.6

(0.049 mmol) of TPPTS in 1.5 ml of H<sub>2</sub>O were dissolved; then, a solution of 2.0 mmol of the substrate of choice in 2 ml of toluene was added. The Schlenk containing the two-phase liquid mixture was transferred to a 150-ml stainless steel autoclave under nitrogen, pressurized to 100 atm with synthesis gas (CO/H<sub>2</sub> = 1) and heated at 100°C for the due time (see tables). The reactor was then cooled to room temperature, the residual gases released, and the reaction mixture analyzed by GLC. The organic phase was separated, toluene removed under vacuum and the aldehydes were recovered and identified as previously described.

### 3. Results and discussion

1,1-Diarylethenes, such as **1** and **2**, were hydroformylated in homogeneous phase in toluene in the presence of rhodium carbonyl complexes under standard conditions (80–120°C; 100 atm [CO/H<sub>2</sub> = 1]) (Scheme 1).

In Table 1, the most representative outcomes from our *oxo*-experiments on olefins **1** and **2** are listed.

Generally, 3,3-diarylpropanals (**6** and **7**) are obtained with high chemo- and regioselectivity [26,28]. Using **1** as the substrate, yields of aldehyde **6** up to 98% are achieved when the hydroformylation is carried out in the presence of

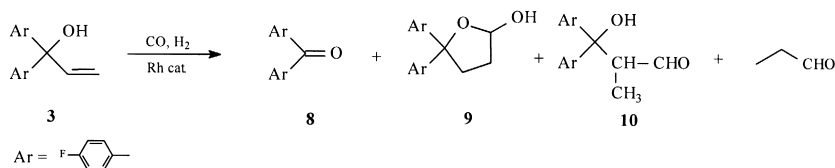
commercially available Rh(CO)<sub>2</sub>(acac) purified just before the use by crystallization from *n*-hexane.

Fluorinated olefin **2** showed to be fairly less reactive towards the *oxo*-reaction under comparable experimental conditions (Table 1): the beneficial effect of using a freshly crystallized sample of Rh(CO)<sub>2</sub>(acac) as the catalyst found in the case of **1** was not observed for this fluorine containing olefin.

Both substrates, **1** and **2**, were subjected to hydroformylation in the biphasic system, toluene/water, using [Rh(COD)Cl]<sub>2</sub>/TPPTS or Rh(CO)<sub>2</sub>(acac)/TPPTS as catalytic systems under analogous reaction conditions.

About the experimental outcomes collected in Table 2, the following remarks can be made:

1. in spite of their low solubility in water, olefins **1** and **2** were smoothly converted into the aldehydes **6** and **7**, respectively, with yield reaching 80–85%;
2. the reaction rate resulted to be fairly lower in the biphasic system with respect to that found in toluene; thus, a temperature of 100°C is suitable to obtain reasonable conversion degrees with similar reaction times;
3. at comparable conversion degrees, analogous chemoselectivity values were found in the homogeneous and in the biphasic *oxo*-reaction;
4. the regioselectivity is affected only to a limited extent by the different reaction medium and is very high in favour of the expected linear aldehyde;
5. the most efficient catalytic system for hydroformylation in water resulted to be [Rh(COD)Cl]<sub>2</sub>/TPPTS.



Scheme 2.

Table 4

Hydroformylation of **3** catalyzed by rhodium complexes in homogeneous phase and in biphasic water/toluene medium

Entry	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion (%)	<i>n</i> -Aldehyde <b>9</b> (%)	<i>i</i> -Aldehyde <b>10</b> (%)	Ketone <b>8</b> + propanal (%)
1 <sup>a</sup>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	15	40	48	32	< 1	15
2 <sup>a</sup>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	5	60	95	72	< 1	22
3 <sup>b</sup>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	24	100	99	71	13	15
4 <sup>b</sup>	Rh(CO) <sub>2</sub> (acac)/TPPTS	24	100	99	77	15	7

<sup>a</sup>Substrate 2 mmol; toluene 3 mL;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 500:1.

<sup>b</sup>Substrate 2 mmol; solvent = 3.5 mL, H<sub>2</sub>O/toluene = 3:4 v/v;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1; Rh/TPPTS molar ratio = 1/3. TPPTS = triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt; COD = 1,5-cyclooctadiene; Hacac = acetylacetonone.

The fact, that the *oxo*-reaction carried out in the biphasic system requires higher temperature, can be due to the rather low concentration of the substrate at the interphase, when only slightly water-soluble olefins are used as substrates.

As in the biphasic *oxo*-reactions a small amount of catalyst can transfer into the organic solvent, we determined, by ICP mass spectrometry, the rhodium content in the toluene phase after the hydroformylation experiments on **1**: 40–50 ppm of this metal were found.

In order to test if the rhodium present in the organic medium is able to hydroformylate this substrate and to get information on the contribution of this reaction to the overall aldehyde yield, we carried out the following control experiment: an *oxo*-reaction on olefin **1** was carried out at 100°C and 100 atm ( $\text{CO}/\text{H}_2 = 1$ ) in the presence of [Rh(COD)Cl]<sub>2</sub>/TPPTS (run 1, Table 3); after 24 h, the organic layer was separated from the aqueous one and allowed to react under the same conditions for further 24 h (run 2, Table 3). Table 3 reports the figures of conversion and selectivity of this experiment.

The conversion degree increase in the second proof is very poor, pointing out that the toluene

solution resulted to display a negligible catalytic activity.

The hydroformylation of **3** in toluene solution catalyzed by rhodium complexes runs particularly well, giving fairly good yields of the linear aldehyde as **9** [27] (Scheme 2).

This compound is a valuable intermediate for the synthesis of a great number of pharmaceuticals including Penfluridol, Pimozide and Lidoflazine [26].

In Table 4, some representative results of our *oxo*-experiments carried out in toluene and in biphasic water/toluene system are collected.

Comparison between the results, listed in Table 4, concerning the *oxo*-reaction carried out in toluene and in biphasic medium shows that: (i) both hydrosoluble catalytic systems afforded satisfactory yields of the desired compound **9**, but it is necessary, with respect to the homogeneous system, to increase the reaction temperature up to 100°C and to prolong the reaction time up to 24 h; (ii) the chemoselectivity is rather high, the total amount of aldehydes in the reaction mixtures achieving about 90%; (iii) the regioselectivity to linear aldehyde, isolated as **9**, does not exceed 76% for both the methodologies employed.

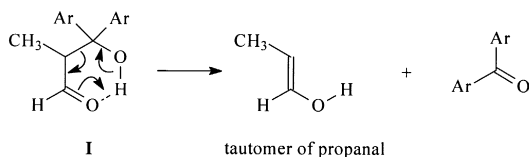
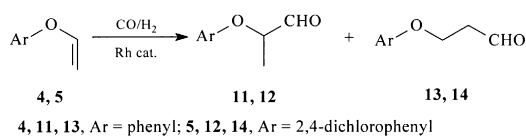


Fig. 2.



4, 11, 13, Ar = phenyl; 5, 12, 14, Ar = 2,4-dichlorophenyl

Scheme 3.

Table 5

Hydroformylation of **4** and **5** catalyzed by rhodium complexes in homogeneous phase<sup>a</sup>

Entry	Substrate	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion (%) <sup>b</sup>	Substrate hydrogenation (%)	Aldehyde yield (%)	Aldehyde selectivity <b>11</b> or <b>12</b> (%)
1	<b>4</b>	Rh <sub>6</sub> (CO) <sub>16</sub>	5	80	99 <sup>c</sup>	3	92	85
2	<b>4</b>	Rh(CO) <sub>2</sub> (acac)	6	80	99	< 1	98	82
3	<b>4</b>	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	12	80	99	2	97	95
4	<b>4</b>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	24	90	92	< 1	91	95
5	<b>5</b>	Rh <sub>6</sub> (CO) <sub>16</sub>	6	80	99	< 1	98	> 99
6	<b>5</b>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	24	80	89	< 1	87	88
7	<b>5</b>	Rh(CO) <sub>2</sub> (acac)	6	80	99	2	97	96

<sup>a</sup>Substrate 2.3 mmol; toluene 5 ml;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1; Rh/P 1:1 molar ratio.<sup>b</sup>Determined by GLC analysis.<sup>c</sup>Four percent phenol.

As far as the chemoselectivity is concerned, it is to point out that ketone (**8**) and propanal are derived from the branched hydroxyaldehyde (**10**) by a retroaldolization reaction as demonstrated by the authors elsewhere [27]. Surprisingly, this reaction seems to take place more easily during the hydroformylation in organic solvent at 60°C than in biphasic system at 100°C. We think that the cleavage of molecule **10**, which occurs under practically neutral conditions ( $\text{pH} = 6.8 \div 7.2$ ), is promoted by heating and involves the cyclic 6-membered intermediate **I**; this reaction, in aqueous phase, occurs in a minor extent, because the hydrogen bonding between the hydroxylic proton and water molecules competes with intramolecular hydrogen bonding between the same proton and the carbonyl oxygen, so perturbing the right geometry of **I** (Fig. 2).

Aryl vinyl ethers represent a very interesting class of substrates for the hydroformylation catalyzed by rhodium complexes, because the branched aldehydes formed are valuable precursors of a variety of 2-aryloxypropanoic acids members of a wide family of herbicides [29].

A large number of rhodium complexes showed to be very efficient catalysts for this reaction (Scheme 3); furthermore, the *oxo*-process is practically regiospecific towards the formation of the desired 2-aryloxypropanals under standard conditions in aromatic solvents [25] (Table 5).

Satisfactory results were achieved also in the hydroformylation of substrates **4** and **5** using the water-soluble catalytic systems, [Rh(COD)Cl]<sub>2</sub>/TPPTS or Rh(CO)<sub>2</sub>(acac)/TPPTS at 100°C and 100 atm ( $\text{CO}/\text{H}_2 = 1$ ); the con-

Table 6

Hydroformylation of **4** and **5** in aqueous biphasic medium<sup>a</sup>

Entry	Substrate	Catalytic precursor	Reaction time (h)	Temperature (°C)	Conversion (%) <sup>b</sup>	Substrate hydrogenation (%)	Aldehyde yield (%)	Aldehyde selectivity <b>11</b> or <b>12</b> (%)
1	<b>4</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	24	100	99	< 1	98	80
2	<b>4</b>	Rh(CO) <sub>2</sub> (acac)/TPPTS	24	100	99 <sup>c</sup>	< 1	95	85
3	<b>5</b>	[Rh(COD)Cl] <sub>2</sub> /TPPTS	24	100	98 <sup>d</sup>	< 1	95	99
4	<b>5</b>	Rh(CO) <sub>2</sub> (acac)/TPPTS	24	100	> 99 <sup>e</sup>	< 1	87	> 99

<sup>a</sup>Substrate 2.8 mmol; solvent = 3.5 ml H<sub>2</sub>O/toluene 3:4;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1; Rh/TPPTS 1:3 molar ratio.<sup>b</sup>Determined by GLC analysis.<sup>c</sup>Three percent phenol.<sup>d</sup>Two percent 2,4-dichlorophenol.<sup>e</sup>Eleven percent 2,4-dichlorophenol. TPPTS = triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt.

Table 7

Recycling of the aqueous phase containing  $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$  in the biphasic hydroformylation of phenyl vinyl ether (**4**)<sup>a</sup>

Entry	Branched aldehyde <b>11</b> (%)	Linear aldehyde <b>13</b> (%)	<b>11/13</b>	Phenol (%)	By-products (%)
1	83.4	7.9	10.6	7.5	1.2
2	83.1	9.0	9.3	6.9	1.0
3	86.9	7.7	11.3	5.1	0.3
4	84.8	8.4	10.1	6.4	0.4

<sup>a</sup>Substrate 2.8 mmol; solvent = 3.5 mL  $\text{H}_2\text{O}/\text{toluene}$  3:4; reaction temperature = 100°C;  $p(\text{CO}) = p(\text{H}_2) = 50$  atm; substrate to catalyst molar ratio 250:1;  $\text{Rh}/\text{TPPTS}$  1:3 molar ratio. In all experiments, nearly quantitative substrate conversions are obtained. TPPTS = triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt.

version degree is comparable with those reached in the homogeneous process; the chemoselectivity, however, is lower because aryl vinyl ethers are cleaved in water phase producing the corresponding phenols (up to 11%) (Table 6).

The regioselectivity towards branched aldehydes **11** or **12** is, however, very high also in this type of catalytic reaction, so that the yield of these *oxo*-products can still range between 85% and 90% (Table 6).

In the case of the hydroformylation of **4**, we have tested the ability of the water-soluble system,  $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ , to maintain its catalytic activity after various *oxo*-experiments. Accordingly, the aqueous phase was separated after the first *oxo*-reaction and reused under the same reaction conditions on the same substrate. Table 7 reports the results obtained in four recycle runs, showing that the catalyst efficiency remains practically unchanged.

#### 4. Conclusion

With the present paper, we have demonstrated that the hydroformylation of slightly water-soluble olefins can be conveniently carried out in a two-phase system in the presence of rhodium carbonyl complexes modified with TPPTS without any addition of co-solvents, hydrophobic auxiliary ligands, or other agents able to improve the transport across the two phases; the drawbacks of higher reaction temperature and occasionally lower chemoselectivities are paid by the easy separation of the catalyst from

the *oxo*-products, by the longer life of the catalyst, and by the utilization of an environmental-friendly solvent. This methodology is particularly useful for the preparation of valuable intermediates to fine-chemicals.

Further research work is currently in progress to find and to test new water-soluble ligands, aiming to achieve more efficient rhodium catalysts.

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