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Journal of Organometallic Chemistry 669 (2003) 172–181
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Hydridorhodium(I) complexes with amphiphilic polyether phosphines
NMR study and biphasic hydroformylation of 1-octene

Antoni Solsona [a], Joan Suades [a,*], René Mathieu [b]

[a] Departament de Química, Edifici C, Universitat Autònoma de Barcelona, Bellaterra, Barcelona 08193, Spain
[b] Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

Received 12 November 2002; received in revised form 20 December 2002; accepted 16 January 2003

Abstract

The formation of hydridorhodium(I) complexes with the amphiphilic phosphines 4-(R)$C_6H_4(OCH_2CH_2)_nPPh_2$ (R = 2,2,4,4-tetramethylbutyl, $n = 1$, $\bar{n} = 5$) was studied by NMR methods and IR spectroscopy. Two approaches were used: (1) the substitution reaction of triphenylphosphine in $RhH(CO)(PPh_3)_3$ by an amphiphilic phosphine and (2) a reaction between the precursor $Rh(acac)(CO)_2$, syngas and the amphiphilic ligand in hydroformylation reaction conditions. Both approaches show the formation of P-coordinated hydridorhodium(I) complexes, and no relevant chelated (P, O) complexes were recognised. The biphasic rhodium-catalysed hydroformylation of 1-octene with the following water-soluble amphiphilic phosphines was studied: 4-(R)$C_6H_4(OCH_2CH_2)_nP(Ph)CH_2CH_2SO_3Na$ (R = 2,2,4,4-tetramethylbutyl, $\bar{n} = 1.4, 5.1, 11.2$; R = *n*-nonyl, $\bar{n} = 1.6, 5.6, 11.4$), and $RP(Ph)CH_2CH_2SO_3Na$ (R = *n*-octyl, $CH_3(OCH_2CH_2)_2OCH_2CH_2$). Ligands with a hydrophobic group and a short polyether chain led to the higher conversion. This result is ascribed to the ability of these ligands to increase the metal concentration in the organic phase.

Keywords: Hydridorhodium(I) complexes; Amphiphilic phosphines; Biphasic hydroformylation

1. Introduction

The synthesis and study of new water-soluble metal complexes for aqueous and biphasic homogeneous catalysis is currently one of the most active research areas in organometallic chemistry [1]. Water-soluble transition metal complexes have been made using functionalised ligands that incorporate polar groups. These hydrophilic complexes can be applied in aqueous biphasic catalysis, since the catalyst is poorly soluble in the organic phase and catalyst recovery is easily rendered by separation of the two phases. An excellent example of this approach is the biphasic Rhurchemie/Rhone-Poulenc process for hydroformylation of propene with the $RhH(CO)(TPPTS)_3$ complex [2]. This biphasic hydroformylation process can also be applied to other olefins, but the reaction rates decrease dramatically by increasing the alkyl chain of the olefin as a result of the poor olefin solubility in the aqueous phase [3]. Several approaches have been proposed to increase the reaction rate in the biphasic hydroformylation of higher olefins as the addition of co-solvents [4], triphenylphosphine [5] or conventional surfactants [6]. In recent years, the use of amphiphilic ligands has been proposed as a new way to attain this goal [7]. The ligands designed for this purpose display, in the same molecule, a long alkyl chain, a hydrophilic group, and one or more donor atoms. Hence, they can form a metallic complex with the properties of a surface-active agent. These compounds act as a bridge between aqueous and organic phases, and lead to accumulation of the metallo-surfactants in the interface and to supramolecular arrangements like micelles or vesicles. In this way, the reaction rate can be improved because

* Corresponding author. Tel.: +34-935-81-2893; fax: +34-935-81-3101.
E-mail address: joan.suades@uab.es (J. Suades).

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doi:10.1016/S0022-328X(03)00040-8

catalyst is accumulated in a high interface surface around the substrate. Most of the reported amphiphilic ligands are functionalised phosphines with hydrophilic sulphonate groups [8], but sulphated [9], phosphonate [10], cationic [11] and non-ionic [12] phosphines have also been reported. In previous papers, we reported the synthesis of a new family of neutral amphiphilic phosphines (ligands **1**–**9**, Scheme 1) [13], and more recently, a new group of anionic amphiphilic phosphines and their palladium metallo-surfactants (ligands **10**–**17**, Scheme 2) have also been described [14].

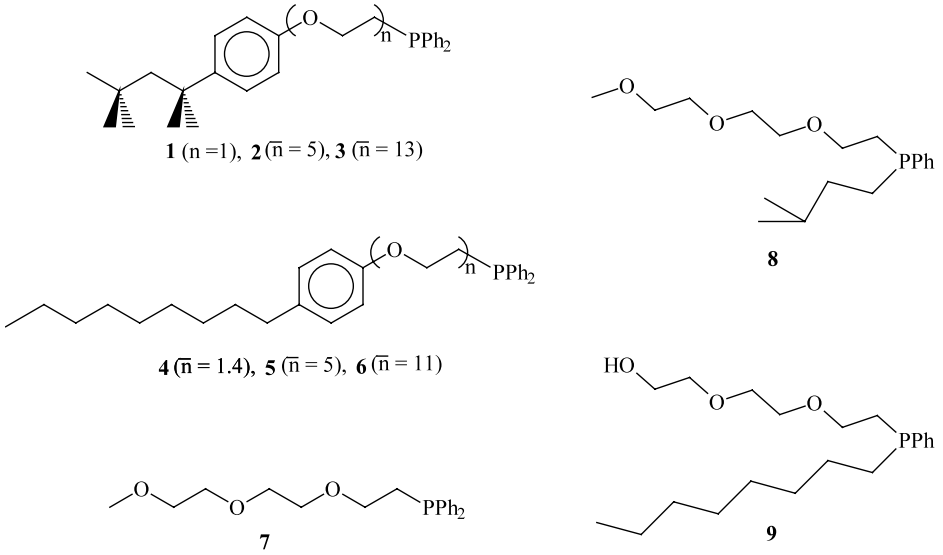
Here, we report: (1) a study of the $[HRh(CO)L_3]$ complexes (L = **1**, **2**) by ^{1}H-, $^{31}P\{^{1}H\}$-, $^{31}P\{^{1}H, ^{103}Rh\}$-, and Ineptnd $^{31}P-^{103}Rh\{^{1}H\}$-NMR spectroscopy. Hydridorhodium complexes were formed in solution from the substitution reaction with $[HRh(CO)(PPh_3)_3]$ or by reaction with $[Rh(acac)(CO)_2]$ and CO/H_2; and (2) a study of biphasic rhodium-catalysed hydroformylation of 1-octene with the amphiphilic ligands **10**–**17**.

2. Results and discussion

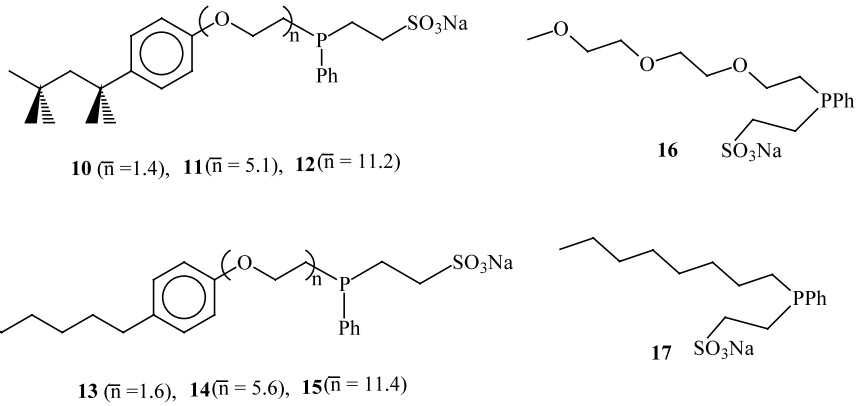
2.1. Hydridorhodium(I) complexes with amphiphilic phosphines

First, the formation of hydridorhodium complexes with the amphiphilic ligands **1**–**17** was studied by means of the known substitution reaction with $HRh(CO)(PPh_3)_3$ (Scheme 3). Unfortunately, preliminary results showed that NMR methods could not supply valuable information about the reaction products with the sulphonated ligands **10**–**17** because only very broad bands were observed. The formation of broad bands with the ligands **10**–**17** has been previously observed and can be assigned to the formation of supramolecular arrangements [14]. This result induced us to focus our attention on the case of non-ionic ligands, and ligands **1** and **2** were retained as model compounds of the reported amphiphilic polyether ligands. Ligand **1** was chosen because it is a molecule where the coordination of the oxygen atom is hindered by electronic and steric influence of the aryl group bonded to this atom. On the contrary, ligand **2** is a compound containing polyether groups which can lead to bidentate (P, O) coordination modes to the metal [13,15].

The reaction of $[HRh(CO)(PPh_3)_3]$ with **1** and **2** was performed in THF with different equivalents of ligand, and the reaction products were analysed by NMR spectroscopy. The ^{1}H- and $^{1}H\{^{31}P\}$-NMR spectra showed unequivocally that a mixture of complexes with the structures displayed in Scheme 4 was formed with both ligands. The ^{1}H spectra display in the hydride region four quadruplets assigned to the hydride of the four structures coupled with the three phosphorus atoms of the ligands (Fig. 1). The $^{1}H\{^{31}P\}$-NMR spectra confirm this assignment since the four signals are now displayed as four singlets. The assignment of these signals to the structures **A**–**D** is also consistent with the changes observed in these spectra in the reaction conducted with one or three equivalents of ligand. Thus, the intensity of signals assigned to the structures **A** and **B** is enhanced in the reaction with one equivalent of ligand, and the signal assigned to **D** is not observed. On the contrary, in the reaction with three equivalents of ligand the signals assigned to structures **C** and **D** are more intense and the signal attributed to **A** is weak. The $^{31}P\{^{1}H\}$-NMR spectroscopy is also in agreement with the formation of the mixture of hydrides shown in Scheme 4, although the interpretation of the spectra is not so straightforward as with the ^{1}H-NMR spectra. Two groups of signals are observed in the 19–24 and



Scheme 1.

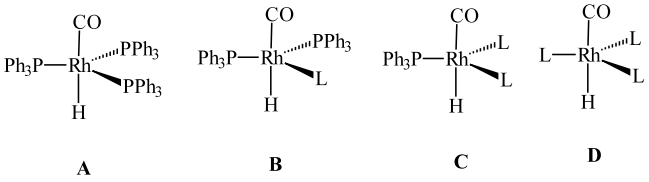


10 ($\overline{n}$ =1.4), **11**($\overline{n}$ = 5.1), **12**($\overline{n}$ = 11.2)

13 ($\overline{n}$ =1.6), **14**($\overline{n}$ = 5.6), **15**($\overline{n}$ = 11.4)

Scheme 2.

39–45 ppm regions, which are respectively assigned to the PPh_2CH_2 and PPh_3 phosphorus atoms coordinated to the metal. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture obtained after reaction of three equivalents of ligand with $HRh(CO)(PPh_3)_3$ is complex, displaying multiple signals as a result of the presence of different compounds with different phosphorus atoms and to the coupling with the rhodium nucleus (Fig. 2). The $^{31}P\{^1H, ^{103}Rh\}$-NMR spectrum was helpful to assign the signals because the absence of coupling with the rhodium nucleus leads to simplified spectra (Fig. 2). Thus, in the 39–45 ppm region of this spectrum a singlet, a doublet, and a triplet were observed. These signals can be respectively assigned to the phosphorus atoms of the PPh_3 in complexes **A**, **B** and **C**, which are respectively coupled with zero, one or two phosphorus atoms of the PPh_2CH_2 groups. The signals of the PPh_2CH_2 groups in the 19–24 ppm region are not so informative because some signals are superposed. However, the doublet of **C** is clearly shown, the triplet of **B** is displayed as one peak and two shoulders, and finally the signal of **D** is observed as a shoulder that is more visible in the $^{31}P\{^1H\}$ spectrum as a doublet. The formation of the four complexes **A**–**D** is also supported by the Ineptnd ^{31}P–$^{103}Rh\{^1H\}$-NMR spectrum, showing the four different rhodium nuclei. The most significant difference (if we compare the $^{31}P\{^1H\}$-NMR spectra obtained after the addition of two equivalents of ligand with the spectra after the addition of three equivalents of ligand) is the intensity enhancement of signals in the region of coordinated triphenylphosphine (39–45 ppm) and the decrease of peaks in the region of coordinated

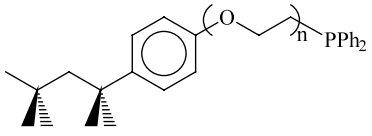


Scheme 4.

PPh_2CH_2 groups (19–24 ppm). This change is a logical consequence of the presence of more triphenylphosphine coordinated to the metal after addition of less amphiphilic phosphine.

For the purpose of achieving information about the hydridorhodium complexes existing when ligands **1** and **2** are employed in the hydroformylation reaction, the reaction between a solution of the complex $[Rh(acac)(CO)_2]$ and ligands **1** and **2** with syngas (20 atm of 1:1 CO/H_2) was studied by NMR and IR spectroscopies (Scheme 5). The reaction was performed by pressurising a THF solution of the precursor $[Rh(acac)(CO)_2]$ and the corresponding ligand with the syngas to 20 atm. This pressurisation was performed in an autoclave which was heated to 50 °C. After reaction, the resulting solution was evaporated to dryness under vacuum and the products were analysed by NMR and IR spectroscopies. In these conditions, the data obtained are in agreement with the formation of the complex $RhH(CO)L_3$ as a main product in the reaction of 1 mol of $[Rh(acac)(CO)_2]$ with 3 mol of ligands **1** and **2**. The ^1H-NMR spectra at room temperature and at low temperature (−60 °C) display a quadruplet as a main signal,

$$\mathbf{HRh(CO)(PPh_3)_3] + 3\ L \longrightarrow [HRh(CO)(PPh_3)_{(3-x)}L_x] + (3\text{-}x)\ L + x\ PPh_3}$$

L = 

Scheme 3.

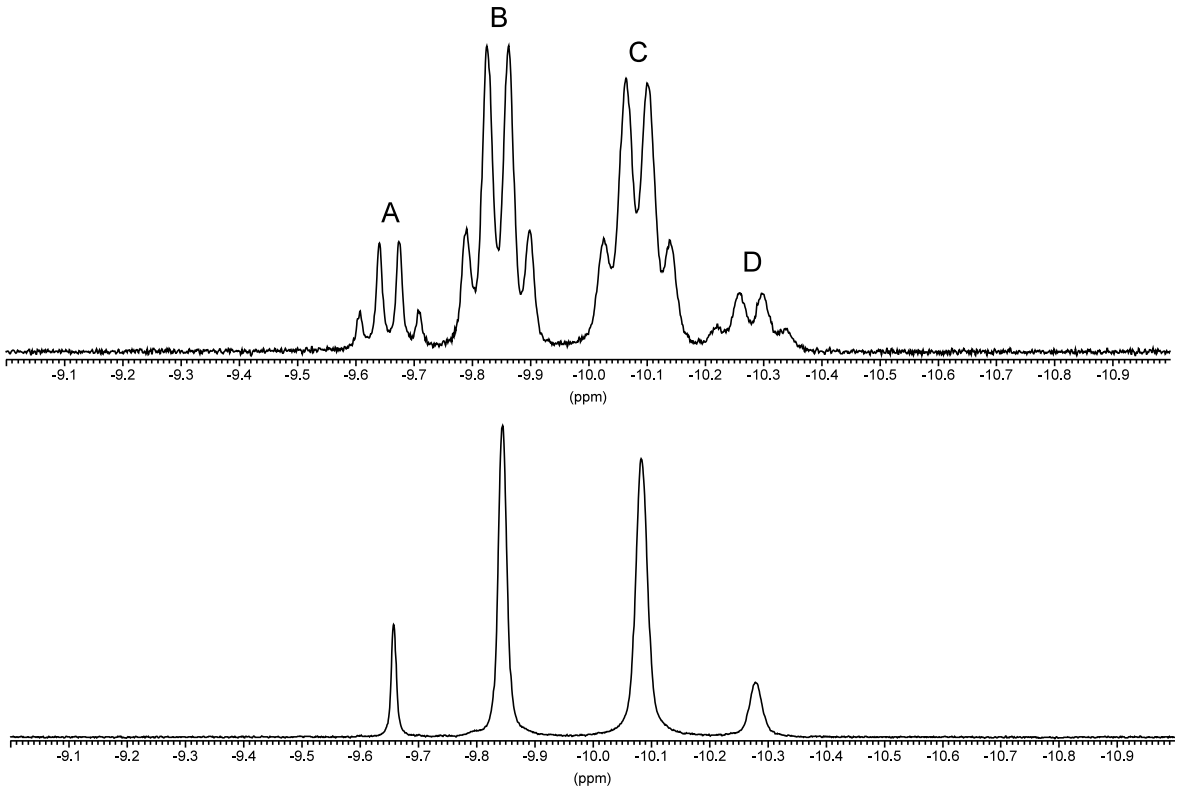


Fig. 1. The ^{1}H-NMR spectrum (CD_2Cl_2, 233 K) after reaction of $HRh(CO)(PPh_3)_3$ with 3 mol of ligand **2**. Top: ^{1}H-NMR spectrum; bottom: $^{1}H\{^{31}P\}$ spectrum.

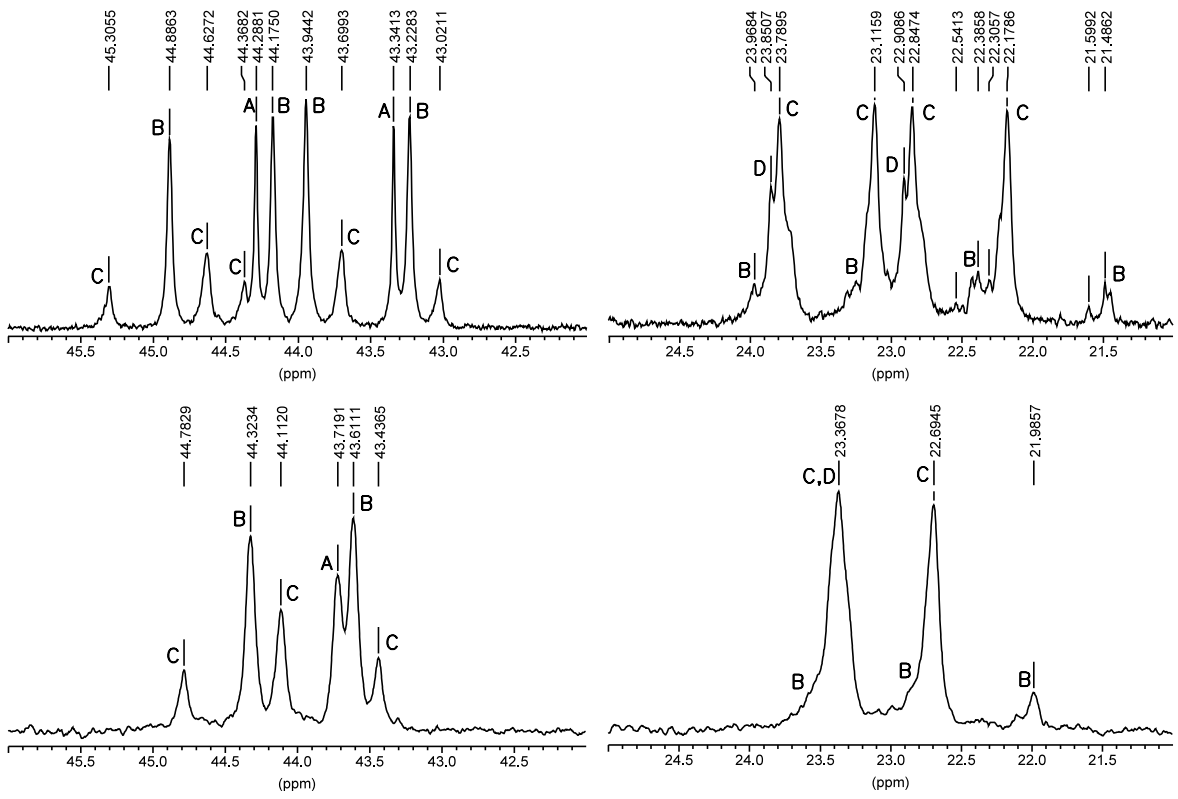
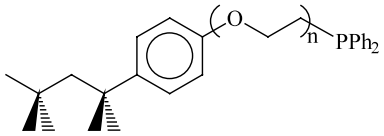


Fig. 2. The ^{31}P-NMR spectrum (CD_2Cl_2, 233 K) after reaction of $HRh(CO)(PPh_3)_3$ with 3 mol of ligand **2**. Top: $^{31}P\{^{1}H\}$-NMR spectrum; bottom: $^{31}P\{^{1}H, ^{103}Rh\}$ spectrum.

$$[Rh(acac)(CO)_2] + 3\,L \xrightarrow[THF]{CO + H_2} [HRh(CO)L_3] + acacH$$

L =



Scheme 5.

with chemical shift and coupling constants nearly identical to those assigned to the complexes RhH(CO)(**1**)$_3$ and RhH(CO)(**2**)$_3$ in the previously described substitution reaction studies with RhH(CO)(PPh_3). The $^1H\{^{31}P\}$-NMR spectra corroborate the coupling of the hydride with three phosphorus nuclei since these signals are now displayed as singlets. The $^{31}P\{^1H\}$-NMR spectra at low temperature are also consistent with these data, and they show a doublet as the main signal, which is also identical to that observed in the substitution reaction with RhH(CO)(PPh_3)$_3$. These spectra also display other weak signals as a peak at −22/−23 ppm assigned to the free ligand and a small doublet at 4.6/4.8 ppm, which can be attributed to the presence of small amounts of dinuclear complexes [16]. The spectra at room temperature do not show significant changes; the doublet assigned to RhH(CO)L_3 (L = **1**, **2**) complexes is also the main signal, and the peak of the free ligand is not observed as a result of a rapid intermolecular exchange processes at higher temperatures. The Ineptnd $^{31}P-^{103}Rh\{^1H\}$-NMR spectra at low temperature exhibits a unique signal with the distinctive quadruplet shape of a rhodium nucleus coupled with three phosphorus atoms for RhH(CO)L_3 (L = **1**, **2**) complexes. The chemical shift and coupling constants of these signals are also very similar to the values obtained in the substitution reaction of Scheme 3. The IR spectra in the ν(C=O) region were examined at the reaction times of 6, 12 and 24 h. These spectra were performed with samples extracted from the autoclave without posterior evaporation, and all of them are nearly identical, displaying two bands at 1976 and 1943 cm^{-1}. The position of these bands is consistent with the reported data for the RhH$(CO)_2(PPh_3)_2$ complex [17]. This result is in accordance with the reported well-known equilibrium between the RhH$(CO)_2L_2$ and RhH(CO)L_3 complexes [16].

The reaction of syngas with a THF solution of [Rh(acac)$(CO)_2$] and ligands **1** and **2** (Scheme 5) was also studied with 2 mol of ligand for each mole of metal. This reaction can supply information about the possible formation of bidentate (P, O) or upper mode of coordination of the amphiphilic ligands to the metal atom. This group of experiments did not lead to NMR spectra with important changes in regard to the previous studies involving the ratio ligand/rhodium = 3. Thus, the ^{1}H-NMR spectra in the hydride region exhibit the signal of the quadruplet attributed to the RhH(CO)L_3 (L = **1**, **2**) complexes, and the $^{31}P\{^1H\}$-NMR spectra display the characteristic doublet of these complexes. Although some minor peaks and broad bands were detected, no significant signals were observed at low fields, as would be expected for the bidentate (P, O) complexes [18].

In conclusion, the complexing studies performed with ligands **1** and **2** show that the complexes formed with these ligands are identical to those reported with other non-functionalised phosphines like PPh_3. Consequently, there is no significant difference between a ligand with unfavourable bidentate (P, O) coordination mode (**1**) and a ligand with favourable bidentate (P, O) coordination mode (**2**). A similar coordination behaviour in the reported amphiphilic ligands with different polyether chain is an attractive idea because it implies that it could be possible to modulate the physical properties (lipophilic character, solubility, etc.) of the complexes involved in catalytic processes by means of changes in the length of the polyether chain without affecting their bonding mode.

2.2. *Two-phase rhodium-catalysed hydroformylation of 1-octene with amphiphilic ligands **10**–**17***

In a previous study, we reported the surfactant properties of ligands **10**–**17** and the metallo-surfactant character of their palladium metal complexes [14]. There, we observed remarkable differences between the surfactant properties of metallo-surfactants with middle polyether chains (**11**, **14**) regarding ligands with long polyether chains (**12**, **15**). Indeed, the metallo-surfactants with middle polyether chains lead to micellar systems where the metal concentration in the interface is higher than in the compounds with longer polyether chains. In order to investigate whether these different surfactant properties can be related to the catalytic properties of metal complexes with the amphiphilic ligands **10**–**17**, studies of two-phase hydroformylation

of 1-octene with rhodium complexes of **10**–**17** were undertaken. The catalyst solutions were prepared by mixing a methanol solution of $Rh(acac)(CO)_2$ with a water solution of the ligand. The experiments were conducted at the temperature of 80 °C and with a 20 atm pressure of syngas, with a ligand-to-rhodium ratio of 10. Catalytic results are summarised in Tables 1 and 2 at substrate-to-metal ratios of 500 and 1000, respectively. For the purposes of comparison, experiments with trisulphonated triphenylphosphine (TPPTS) were also performed in order to have available catalytic data of a non-amphiphilic but water-soluble ligand in identical experimental conditions. In general, in the assays with high conversion a relevant activity was observed for alcohol formation [8b]. The yields of nonanols with respect to the total products are displayed in the last column. Since we used methanol as a co-solvent, acetals formation is a possible side reaction between aldehydes and methanol. This reaction was only significant in the assays of Table 1 with higher conversion, which corresponds to TPPTS (3.3% formation of acetals) and **13** (5.6% formation of acetals). Other side reactions such as hydrogenation and isomerisation were minor, with yields lower than 1% in most cases, and with the logical exception of experiments with very low conversion (**16** and **17**), where the hydrogenation increases to 10% of products.

The analysis of conversion data displayed in Tables 1 and 2 shows that all catalysts prepared with ligands with middle (**11**, **14**, **16**) or long polyether chains (**12**, **15**) exhibit poorer conversion results than the assays with TPPTS. Conversely, the conversion in experiments performed with ligands with a hydrophobic group and a short polyether chain (**10**, **13**) is seen to be significantly higher than with other ligands. In fact, ligand **13** shows higher conversion than TPPTS in Table 1 and comparable data in Table 2. The special activity of ligands **10** and **13** can probably be attributed to the ability of these ligands to increase the metal concentration in the organic phase. Indeed, the two-phase system after hydroformylation reaction showed an intense coloration of the organic phase in the experiments performed with ligands **10** and **13**. Likewise, the sole ligands (**16**, **17**), which led to a two-phase system after hydroformylation reaction with the organic phase absolutely colourless, coincide with the experiments with the lower conversion results. As mentioned earlier, the interest of biphasic catalysis is to obtain a catalyst that is poorly soluble in the organic phase but which can be easily recovered by separation of the two phases. As a conclusion, the demonstrated surfactant properties of ligands **10**–**17** do not involve an improvement of the catalytic biphasic hydroformylation reaction in the studied reaction conditions because the observed activity seems to be related to the metal transfer into the organic phase.

3. Experimental

3.1. General

All reactions were performed under nitrogen by standard Schlenk tube techniques. Solvents were purified by standard procedures. The NMR spectra were recorded by the Service de RMN du Laboratoire de Chimie de Coordination on Bruker AC250 and AMX-400 instruments. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvents for ^1H spectra, to solvent signals for ^{13}C spectra and to external phosphoric acid for ^{31}P spectra.

The hydroformylation reactions were performed in a 125 ml stainless steel autoclave of Autoclave Engineers equipped with mechanical stirring and temperature controller. The solution was contained in a glass inlet. The pressure of the autoclave was kept constant by means of a regulator, connected to a syngas reservoir. The evolution of the reaction was monitored by the drop of pressure in the reservoir. Conversions and regioselec-

Table 1
Two-phase hydroformylation of 1-octene with rhodium catalyst (1-octene/Rh = 500)

Ligand	Conversion [a] (%)	Aldehydes + alcohols [b] (%)	Regioselectivity [c] (%)	Nonanol (%)
TPPTS	91	97	80	0.5
10	50	100	78	14
11	25	96	76	6.4
12	31	95	72	4.3
13	97	100	73	12.7
14	28	100	75	10.7
15	25	100	70	2.9
16	5	80	70	–
17	6	83	72	–

Reaction conditions: 25 mmol of 1-octene, 0.05 mmol of $[Rh(acac)(CO)_2]$, and 0.50 mmol of ligand; temperature: 80 °C; and reaction time: 24 h.
[a] Converted olefin as percentage of the initial amount.
[b] Percentage of aldehydes plus alcohols relative to the converted olefin.
[c] Percentage of linear aldehydes plus alcohols.

Table 2
Two-phase hydroformylation of 1-octene with rhodium catalyst (1-octene/Rh = 1000)

Ligand	Conversion [a] (%)	Aldehydes + alcohols [b] (%)	Regioselectivity [c] (%)	Nonanol (%)
TPPTS	68	90	76	–
10	42	98	77	–
11	4	75	70	–
12	12	92	68	–
13	60	98	71	3.2
14	4	85	71	
15	10	95	69	
17	5	80	71	–

Reaction conditions: 25 mmol of 1-octene, 0.025 mmol of [Rh(acac)$(CO)_2$], and 0.25 mmol of ligand; temperature: 80 °C; and reaction time: 24 h.
[a] Converted olefin as percentage of the initial amount.
[b] Percentage of aldehydes plus alcohols relative to the converted olefin.
[c] Percentage of linear aldehydes plus alcohols.

tivity were determined by gas chromatography with a Hewlett-Packard G1800A, equipped with a capillary HP5 column (30 m × 0.25 mm). The reaction products were identified by comparison with authentic samples and mass spectroscopy. Compounds [RhH(CO)$(PPh_3)_3$] [19] and [Rh(acac)$(CO)_2$] [20] were prepared by published procedures.

3.2. Complexation studies with [RhH(CO)$(PPh_3)_3$]

The following procedure was used in all experiments with ligands **1** and **2**. To a solution of [RhH(CO)$(PPh_3)_3$] (0.100 g, 0.11 mmol) in THF (30 ml), 0.11, 0.22 or 0.33 mmol of the respective phosphines was slowly added with continuous stirring. The resulting solutions were stirred for 12 h and evaporated to dryness in vacuum leading to red oils, which were used to measure the $^{31}P\{^1H\}$- and ^1H-NMR spectra.

3.2.1. Studies with ligand *1*

a) Reaction with one equivalent of ligand (L/Rh = 1): ^1H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −9.78 (b, Rh*H*(CO)$(PPh_3)L_2$), −9.53 (br q, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)$(PPh_3)_2L$), −9.27 (b, Rh*H*(CO)$(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.67 (b, CH_2–P), 4.11 (b, CH_2O).
$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): −5.0 (b, PPh_3), 19–23 (weak signals of the coordinated PPh_2 groups of ligand **1**), 40.9 (d, $^1J_{PRh} = 153.8$ Hz, RhH(CO)$(PPh_3)_3$), 41.1 (dd, $^1J_{PRh} = 151.4$ Hz, $^2J_{PP} = 117.2$ Hz, RhH(CO)$(PPh_3)_2L$).

b) Reaction with two equivalents of ligand (L/Rh = 2): ^1H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −9.97 (partially hidden weak signal with quadruplet shape, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)L_3), −9.78 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)$(PPh_3)L_2$), −9.53 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)$(PPh_3)_2L$), −9.27 (b, Rh*H*(CO)$(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 4.2 (b, CH_2O).
$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): −4.9 (b, PPh_3), 21.8 (dd, $^1J_{PRh} = 153.8$ Hz, $^2J_{PP} = 107.5$ Hz, RhH(CO)$(PPh_3)(PPh_2R)_2$), 22.3 (d, $^1J_{PRh} = 151.4$ Hz, RhH(CO)$(PPh_2R)_3$), 40.9 (d, $^1J_{PRh} = 153.8$ Hz, RhH(CO)$(PPh_3)_3$), 41.1 (dd, $^1J_{PRh} = 151.4$ Hz, $^2J_{PP} = 117.2$ Hz, RhH(CO)$(PPh_3)_2L$). In the 19–24 ppm region are observed some weak signals assigned to the coordinated PPh_2R groups of complex RhH(CO)$(PPh_3)_2L$. Likewise, some weak peaks assigned to the coordinated PPh_3 of RhH(CO)$(PPh_3)L_2$ are observed in the 39–45 ppm region.

c) Reaction with three equivalents of ligand (L/Rh = 3): ^1H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −9.97 (partially hidden weak signal with quadruplet shape, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)L_3), −9.78 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)$(PPh_3)L_2$), −9.53 (broad signal with quadruplet shape, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)$(PPh_3)_2L$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 4.2 (b, CH_2O).
$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): −17.0 (b, PPh_2R), −4.9 (s, PPh_3), 21.8 (dd, $^1J_{PRh} = 153.8$ Hz, $^2J_{PP} = 107.5$ Hz, RhH(CO)$(PPh_3)(PPh_2R)_2$), 22.3 (d, $^1J_{PRh} = 151.4$ Hz, RhH(CO)$(PPh_2R)_3$), 39–45 (weak signals assigned to the coordinated PPh_3).

3.2.2. Studies with ligand *2*

a) Reaction with two equivalents of ligand (L/Rh = 2): ^1H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.09 (partially hidden weak signal with quadruplet shape, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)L_3), −9.86 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)$(PPh_3)L_2$), −9.58 (br q, $^2J_{HP} \approx 15$ Hz, Rh*H*(CO)$(PPh_3)_2L$), −9.32 (b, RhH(CO)$(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl),

2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O).

$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): −4.6 (b, PPh_3), 21.5 (dd, $^1J_{PRh} = 151.4$ Hz, $^2J_{PP} = 105.0$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$), 40.9 (d, $^1J_{PRh} = 153.9$, $RhH(CO)(PPh_3)_3$), 41.1 (dd, $^1J_{PRh} = 151.7$ Hz, $^2J_{PP} = 117.2$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$). Some weak signals and shoulders were observed between 19–24 ppm and 39–45 ppm which were respectively assigned to $RhH(CO)(PPh_3)_2(PPh_2R)$ and $RhH(CO)(PPh_3)(PPh_2R)_2$.

b) Reaction with three equivalents of ligand (L/Rh = 2): ^{1}H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.09 (weak signal with quadruplet shape partially hidden, $^2J_{HP} = 15.0$ Hz, $RhH(CO)L_3$), −9.87 (q, $^2J_{HP} = 14.7$ Hz, $RhH(CO)(PPh_3)L_2$), −9.58 (br q, $^2J_{HP} \approx 15$ Hz, $RhH(CO)(PPh_3)_2L$), −9.32 (b, $RhH(CO)(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O).

$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): −4.9 (b, PPh_3), 21.5 (dd, $^1J_{PRh} = 151.4$ Hz, $^2J_{PP} = 105.0$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$), 40.9 (d, $^1J_{PRh} = 153.9$, $RhH(CO)(PPh_3)_3$), 41.1 (dd, $^1J_{PRh} = 151.7$ Hz, $^2J_{PP} = 117.2$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$). Some weak signals and shoulders were observed between 19–24 ppm and 39–45 ppm which were respectively assigned to $RhH(CO)(PPh_3)_2(PPh_2R)$ and $RhH(CO)(PPh_3)(PPh_2R)_2$.

c) Reaction with three equivalents of ligand (L/Rh = 2) at 233 K (these spectra were recorded in an AMX-400 instrument). ^{1}H-NMR ($T = 233$ K; CD_2Cl_2; except phenyl resonances): −10.28 (q, $^2J_{HP} = 15.6$ Hz, $RhH(CO)L_3$), −10.09 (q, $^2J_{HP} = 15.2$ Hz, $RhH(CO)(PPh_3)L_2$), −9.85 (q, $^2J_{HP} = 14.6$ Hz, $RhH(CO)(PPh_3)_2L$), −9.67 (q, $^2J_{HP} = 13.2$ Hz, $RhH(CO)(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.37 (s, $(CH_3)_2$), 1.75 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 3.9 (b, CH_2O).

$^1H\{^{31}P\}$-NMR ($T = 233$ K; CD_2Cl_2; except phenyl resonances): −10.28 (s, $RhH(CO)L_3$), −10.09 (s, $RhH(CO)(PPh_3)L_2$), −9.85 (s, $RhH(CO)(PPh_3)_2L$), −9.67 (s, $RhH(CO)(PPh_3)_3$), 0.75 (s, $(CH_3)_3$), 1.37 (s, $(CH_3)_2$), 1.75 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 3.9 (b, CH_2O).

$^{31}P\{^1H\}$-NMR ($T = 233$ K; CD_2Cl_2): 22.98 (dd, $^1J_{PRh} = 152.2$ Hz, $^2J_{PP} = 108.5$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$), 23.38 (d, $^1J_{PRh} = 152.6$ Hz, $RhH(CO)(PPh_2R)_3$), 43.81 (d, $^1J_{PRh} = 153.8$ Hz, $RhH(CO)(PPh_3)_3$), 44.05 (dd, $^1J_{PRh} = 152.6$ Hz, $^2J_{PP} = 115.5$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$), 44.16 (dt, $^1J_{PRh} = 150.3$ Hz, $^2J_{PP} = 109.8$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$). Some weak signals and shoulders were observed between 21 and 24 ppm, which were assigned to $RhH(CO)(PPh_3)_2(PPh_2R)$.

$^{31}P\{^1H, ^{103}Rh\}$-NMR ($T = 233$ K; CD_2Cl_2): 22.8 (t(sh), $^2J_{PP} \approx 125$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$), 23.03 (d, $^2J_{PP} = 108.5$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$), 23.38 (s(sh), $RhH(CO)(PPh_2R)_3$), 43.72 (s, $RhH(CO)(PPh_3)_3$), 43.98 (d, $^2J_{PP} = 115.5$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$), 44.11 (t, $^2J_{PP} = 109.8$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$).

Ineptnd $^{31}P-^{103}Rh\{^1H\}$-NMR ($T = 233$ K; CD_2Cl_2): −885.9 (q, $^1J_{PRh} = 150.1$ Hz, $RhH(CO)(PPh_2R)_3$), −864.7 (q, $^1J_{PRh} = 150.6$ Hz, $RhH(CO)(PPh_3)(PPh_2R)_2$), −842.0 (q, $^1J_{PRh} = 150.1$ Hz, $RhH(CO)(PPh_3)_2(PPh_2R)$), −820.2 (q, $^1J_{PRh} = 153.3$ Hz, $RhH(CO)(PPh_3)_3$).

3.3. Complexation studies with [Rh(acac)(CO)$_2$]

The following procedure was used in all experiments with ligands **1** and **2** with the L/Rh ratios of 2 and 3. To a solution of [Rh(acac)$(CO)_2$] (0.100 g, 0.39 mmol) in THF (20 ml) was added 0.78 or 1.17 mmol of the respective phosphine with continuous stirring. The resulting solution was transferred under nitrogen to an autoclave, pressurised to 20 atm with syngas ($CO + H_2$), heated to 50 °C and allowed under stirring for 24 h. Next, the system was cooled, depressurised and the reaction mixture was transferred under nitrogen to an Schlenk tube. The resulting solutions were evaporated to dryness in vacuo yielding dark oils, which were used to measure the $^{31}P\{^1H\}$- and ^{1}H-NMR spectra. The IR spectra in the ν(C=O) region were measured at the reaction times of 6, 12 and 24 h for all experiments. All recorded spectra display two peaks at 1976 and 1943 cm^{-1} ($RhH(CO)_2L_2$).

3.3.1. Significant NMR data

3.3.1.1. Studies with ligand *1*.

a) Reaction with two equivalents of ligand (L/Rh = 2): ^{1}H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.02 (q, $^2J_{HP} = 15.6$, $RhH(CO)L_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.64 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 4.1 (b, CH_2O).

$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): 22.3 (d, $^1J_{PRh} = 151.4$ Hz, $RhH(CO)(PPh_2R)_3$). Two unassigned broad signals were observed at 18.0 and 28.7 ppm.

b) Reaction with three equivalents of ligand (L/Rh = 3): ^{1}H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.04 (q, $^2J_{HP} = 15.0$ Hz, $RhH(CO)L_3$), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.64 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.7 (b, CH_2–P), 4.1 (b, CH_2O).

$^{31}P\{^1H\}$-NMR ($T = 298$ K; C_6D_6): 22.3 (d, $^1J_{PRh} = 151.4$ Hz, $RhH(CO)(PPh_2R)_3$). A very weak unassigned doublets were observed at 4.8 ppm ($^1J_{PRh} = 156.3$ Hz).

c) Reaction with three equivalents of ligand (L/Rh = 3) at 213 K (these spectra were recorded in an AMX-400 instrument): ^{1}H-NMR ($T = 213$ K; CD_2Cl_2; except phenyl resonances): −10.19 (q, $^2J_{HP} = 15.6$ Hz, Rh*H*(CO)L_3), 0.63 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.67 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.53 (b, CH_2–P–Rh), 2.62 (b, CH_2–P), 3.7 (b, OC*H*$_2$CH$_2$P–Rh), 4.1 (b, OC*H*$_2$CH$_2$P–Rh). An unassigned broad band is observed at −12.6 ppm.

^{1}H{^{31}P}-NMR ($T = 213$ K; CD_2Cl_2; except phenyl resonances): −10.19 (s, Rh*H*(CO)L_3), 0.63 (s, $(CH_3)_3$), 1.27 (s, $(CH_3)_2$), 1.67 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.53 (b, CH_2–P–Rh), 2.62 (b, CH_2–P), 3.7 (b, OC*H*$_2$CH$_2$P–Rh), 4.1 (b, OC*H*$_2$CH$_2$P–Rh). An unassigned broad band is observed at −12.6 ppm.

^{31}P{^{1}H}-NMR ($T = 213$ K; CD_2Cl_2): −23.0 (s, PPh_2R), 23.7 (d, $^1J_{PRh} = 151.4$ Hz, RhH(CO)-(*P*$Ph_2R)_3$).

Ineptnd ^{31}P–^{103}Rh{^{1}H}-NMR ($T = 213$ K; CD_2Cl_2): −899.8 (q, $^1J_{PRh} = 150.9$ Hz, *Rh*H(CO)-$(PPh_2R)_3$).

3.3.1.2. Studies with ligand ***2****.*

a) Reaction with two equivalents of ligand (L/Rh = 2): ^{1}H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.12 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)L_3), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O).

^{31}P{^{1}H}-NMR ($T = 298$ K; C_6D_6): 21.9 (d, $^1J_{PRh} = 151.4$ Hz, RhH(CO)(*P*$Ph_2R)_3$). A weak unassigned doublet is observed at 4.6 ppm ($^1J_{PRh} = 156.3$ Hz).

b) Reaction with three equivalents of ligand (L/Rh = 3): ^{1}H-NMR ($T = 298$ K; C_6D_6; except phenyl resonances): −10.12 (q, $^2J_{HP} = 15.0$ Hz, Rh*H*(CO)L_3), 0.75 (s, $(CH_3)_3$), 1.28 (s, $(CH_3)_2$), 1.65 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O).

^{31}P{^{1}H}-NMR ($T = 298$ K; C_6D_6): 21.9 (d, $^1J_{PRh} = 151.4$ Hz, RhH(CO)(*P*$Ph_2R)_3$). A weak unassigned doublet is observed at 4.6 ppm ($^1J_{PRh} = 156.3$ Hz).

c) Reaction with three equivalents of ligand (L/Rh = 3) at 213 K (these spectra were recorded in an AMX-400 instrument): ^{1}H-NMR ($T = 213$ K; CD_2Cl_2; except phenyl resonances): −10.40 (q, $^2J_{HP} = 15.5$ Hz, Rh*H*(CO)L_3), 0.63 (s, $(CH_3)_3$), 1.29 (s, $(CH_3)_2$), 1.67 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O). A weak unassigned broad signal was observed at −12.5 ppm.

^{1}H{^{31}P}-NMR ($T = 213$ K; CD_2Cl_2; except phenyl resonances): −10.40 (s, Rh*H*(CO)L_3), 0.63 (s, $(CH_3)_3$), 1.29 (s, $(CH_3)_2$), 1.67 (s, CH_2, 2,2,4,4-tetramethylbutyl), 2.6 (b, CH_2–P), 3.1–4.0 (m, CH_2O). A weak unassigned broad signal was observed at −12.5 ppm.

^{31}P{^{1}H}-NMR ($T = 213$ K; CD_2Cl_2): −22.0 (b, PPh_2R), 23.1 (d, $^1J_{PRh} = 151.1$ Hz, RhH(CO)-(*P*$Ph_2R)_3$). A weak unassigned doublet was observed at 4.9 ppm (d, $^1J_{PRh} = 158.0$ Hz).

Ineptnd ^{31}P–^{103}Rh{^{1}H}-NMR ($T = 213$ K; CD_2Cl_2): −886.3 (q, $^1J_{PRh} = 151.3$ Hz, *Rh*H(CO)-$(PPh_2R)_3$).

3.4. Catalytic hydroformylation of 1-octene: general procedure

A solution of [Rh(acac)(CO)$_2$] in methanol (5 ml) was prepared with slight heating in order to achieve solid dissolution. This solution was added to a solution of the desired amount of the phosphine (0.25/0.50 mmol) in water (5 ml). The resulting solution was stirred for 10 min and a yellowish-orange solution was obtained. Next, 1-octene was added (4 ml) and the resulting mixture was transferred to the evacuated autoclave, which was pressurised up to 15 atm and heated to 80 °C under stirring at 50 rpm. When the thermal equilibrium was reached, the pressure was adjusted to 20 atm and the stirring to 400 rpm. This moment was defined as reaction time equal to zero.

Acknowledgements

The authors thank DGICYT (Programa de Promoción General del Conocimiento) for financial support.

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