

A new, highly selective, water-soluble rhodium catalyst for methyl acrylate hydroformylation

Georges Fremy^a, Yves Castanet^a, Ryszard Grzybek^b, Eric Monflier^c, André Mortreux^{a,*}, Anna M. Trzeciak^d, Jozef J. Ziolkowski^{d,*}

^a Laboratoire de Catalyse Homogène et Hétérogène, URA CNRS 402, ENSCL, Bâtiment C7, B.P. 108-59652, Villeneuve d'Ascq Cedex, France

^b Institute of Chemistry, Silesian University, 9 Szkolna Street, 40-006 Katowice, Poland

^c Université d'Artois, Faculté des Sciences J. Perrin, Rue Jean Souvraz, Sac Postal 18, 62307-Lens Cedex, France

^d Institute of Chemistry, Wrocław University, 14 Joliot-Curie Street, 50-383 Wrocław, Poland

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Abstract

Hydroformylation of methylacrylate to α -aldehyde can be achieved in a two-phase system in the presence of two new water-soluble phosphines. High yields and selectivities of α -aldehyde (ca. 80% with a α/β ratio of 1:20) were obtained. Spectroscopic studies have been carried out and some new rhodium complexes formed in situ in catalytic systems have been identified.

Keywords: Hydroformylation; Methyl acrylate; Water-soluble phosphines; Rhodium; Catalysis; Two phase system

1. Introduction

In transition-metal catalysed reactions, the high price of the catalyst makes it necessary to prevent losses of the precious metal and to separate the reaction products from the catalyst system with minimum impairment of the catalyst properties.

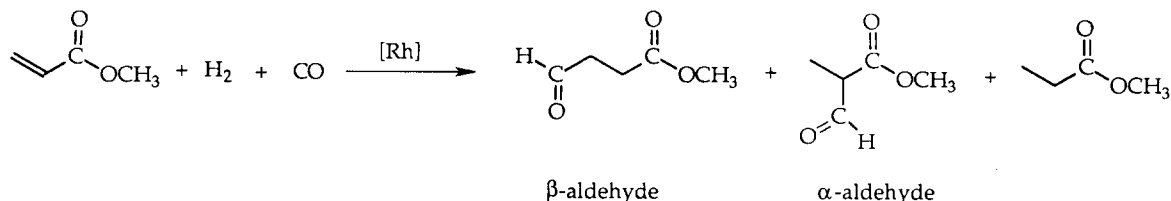
Two-phase systems containing a catalyst soluble in an aqueous or fluorous¹ phase and an organic phase in which both reaction substrates and products are soluble are of great interest [1,2].

Reactions in water solution or in aqueous–organic two-phase systems are possible when ligands and metal complexes are water soluble [1]. In these two-phase systems, the use of surfactants (i.e. ammonium salts) [3] or amphiphilic ligands [4] is also required to obtain good activities when substrates are totally water-insoluble. The more common water-soluble phosphines are phenylphosphines with polar functional groups attached to phenyl ring ($-\text{SO}_3^-$; $-\text{CO}_2^-$; $-\text{NR}_3^+$) [1,2]. Usually, phosphites are not used in such systems because of their

easy hydrolysis. However, it was recently found that appropriately modified phosphites are quite stable in water [5]. Sulphonated phosphines have been studied particularly [6–13], and one of them, the trisulphonated triphenylphosphine (TPPTS), is even used for propylene hydroformylation on an industrial scale (Ruhrchemie/Rhône-Poulenc) [14]. $[\text{Rh}(\text{acac})(\text{CO})_2]$ with various water-soluble monodentate phosphines such as $\text{P}[(\text{CH}_2)_n\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3$, $\text{P}[\text{C}_6\text{H}_4(\text{CH}_2)_n\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3$, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SO}_3\text{Na}$ and $\text{P}(\text{C}_6\text{H}_3\text{FSO}_3\text{Na})_3$ was found to be a very active catalyst for olefin hydroformylation [15,16]. Rhodium(III) acetate or $[\text{Rh}(\text{acac})(\text{CO})_2]$, modified with sulphonated diphosphines, such as the sulphonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBISNa) and 1,2-bis[di(*m*-sodiosulphonatophenyl)phosphino]ethane (DPPETS), produce active catalysts for propylene and 1-octene hydroformylation [17]. Chiral sulphonated diphosphines also produce stereoselective catalysts for olefin hydrogenation [18,19]. Some rhodium complexes with sulphonated phosphines, such as $[\text{Rh}_2(\mu\text{-SBU}^1)_2(\text{CO})_2(\text{TPPTS})_2]$ are catalytically active in the water gas shift reaction and may be also used as hydroformylation catalysts [20]. Metal complexes with ligands containing quaternary nitrogen, such as amphos, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3^+$ [20,21] or quaternary phosphorus, such as phosphos, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PMe}_3^+$

* Corresponding authors.

¹ “Fluorous” has been used to indicate the fluorocarbon-rich phase of a biphasic system [1b].



Scheme 1. Rhodium-catalysed hydroformylation of methyl acrylate.

[23,24] may be also used, both in water and in two-phase systems.

In this paper, we report our results on methylacrylate hydroformylation in one- and two-phase systems with new water-soluble phosphines (Scheme 1).

Hydroformylation of methyl acrylate to α -branched aldehyde is a very useful reaction. 3-Hydroxy-2-methylpropanoic acid derivatives obtained by enzymatic hydrogenation of the racemic α -branched aldehyde are very important chiral building blocks [25]. Rhodium(I) complexes with new water-soluble phosphines PNS and PC (Scheme 2) were used as the catalyst precursors [26]. Studies of spectroscopy and catalytic activity have been carried out and some new rhodium complexes formed in situ in the catalytic systems have been identified.

2. Experimental section

2.1. Materials

Methyl acrylate was purchased from Aldrich and deoxygenated prior to use. Tetrahydrofuran (THF), toluene and diethyl ether were purchased from Janssen and were distilled prior to use. [3-(sodium sulphonato)phenyl] diphenylphosphine (TPPMS) was synthesised according to published procedures [27]. Distilled deionised water was used and $[\text{Rh}(\text{acac})(\text{CO})_2]$ obtained from Strem (98% pure) was employed in all the cat-

alytic reactions. CO/H_2 (50/50) was from Air-Liquide and used without further purification.

2.2. Apparatus

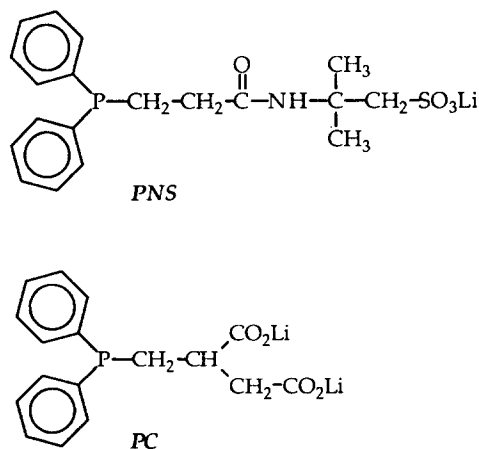
IR spectra were determined with an FTIR Nicolet Impact 400 spectrometer. For FTIR spectra in water, a CaF_2 cell was used. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained at 25°C with Bruker 300 and Varian VXR 300 spectrometers at observation frequencies of 300, 75.45 and 121.5 MHz, respectively. Hydrogen-1 and carbon-13 chemical shifts were referenced to external tetramethylsilane. Phosphorus-31 chemical shifts were referenced to external 85% H_3PO_4 .

All synthesis and catalytic reactions were performed under dinitrogen using standard Schlenk techniques. The catalytic reactions were carried out in a stainless steel 100 ml autoclave reactor equipped with arrangements for automatic temperature control and variable mechanical stirrer speeds. A rupture safety disc was also fitted to the reactor. In order to keep constant the CO/H_2 pressure, a gas reservoir was used with a constant-pressure regulator. Reaction products and starting materials were determined by gas chromatography on a Chrompack 9001 chromatograph equipped with a CPSIL 5 CB column $25\text{ m} \times 0.32\text{ mm}$ and FID detector.

2.3. Experimental procedure for synthesis of new water soluble phosphines [26]

2.3.1. Synthesis of *N*-[1',1'-dimethyl-2'-ethanesulfonate]-diphenylphosphine-3-propanamide, lithium salt (PNS)

To 13.5 g of triphenylphosphine in 50 ml of THF and 1 g of metallic lithium was added and stirred for 6 h. The solution, separated from the unreacted lithium metal, was slowly diluted with ca. 20 ml of THF, and 10.35 g of $\text{CH}_2=\text{CH}-\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{H}$ dissolved in 50 ml of THF at 20°C was slowly added. The solution obtained was stirred for 1 h and then quickly added to 250 ml of diethyl ether. The precipitate obtained was characterised as $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CONHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{Li}$ (PNS) in 98% yield. ^1H NMR/ D_2O : δ (ppm) 1.3 (6H, CH_3); 2.2 (4H, CH_2); 3.3 (2H, CH_2); 7.3 (10H, Ph). ^{13}C NMR/ D_2O : δ (ppm) 25.7 (CH_2), 29.1 (CH_3), 35.7 (CH_2), 54.7 ($-\text{C}(\text{CH}_3)_2-$), 60.5 ($\text{CH}_2-\text{C}(\text{O})$),



Scheme 2. New water-soluble phosphines PNS and PC.

Table 1

Methylacrylate hydroformylation in various solvents at 10 bar of CO/H₂^a

Entry	Phosphine	Phosphine/ rhodium ratio	methylacrylate/ rhodium ratio	Solvent	Time (h)	Conversion (mol%)	α -Aldehyde yield (mol%)	Methylpropionate yield (mol%)
1	PNS	4	210	water	24	40	0	40
2	PPh ₃	4.5	210	toluene ^b	4.5	40	2	38
3	PNS	4	210	toluene	5	100	12	88
4	PNS	2	480	toluene	8	34	6	28
5	PNS	4	210	THF	7	100	21	79
6	PNS	4	480	THF	8	100	20	80
7	PNS	4	210	toluene/water ^c	20	100	13	87
8	PNS	4	480	toluene/water ^c	20	35	5	30
9	PNS	2	210	toluene/water ^c	20	100	15	85

^a Reaction conditions: [Rh(acac)(CO)₂] 0.02 mmol; Solvent: 2.5 ml; T 80°C; P_{CO/H₂} = 10 bar (CO/H₂ = 1:1).^b toluene; 1 ml.^c toluene/water 2/0.5 ml.

131.3 (Ph), 131.4 (Ph), 131.5 (Ph), 135.2 (Ph), 135.4 (Ph), 176.4 (C(O)). ³¹P NMR/D₂O: δ (ppm) –17. IR/KBr (cm^{–1}): 1642 (CO) 1539, 1432, 1218 (SO₃), 1068, 741, 700/Nujol (cm^{–1}): 3400 (NH).

2.3.2. Synthesis of diphenylphosphinomethyl-2-succinate, dilithium salt (PC)

A suspension of 1 g of metallic lithium in 50 ml of THF containing 13.5 g of triphenylphosphine was stirred for 6 h. The solution, separated from the unreacted lithium metal was diluted with ca. 20 ml of THF, and 6.7 g of itaconic acid (CH₂=CH(COOH)(CH₂COOH)) dissolved in 50 ml of THF was slowly added at 20°C. The solution obtained was stirred for 1 h and then quickly added to 250 ml of diethyl ether. The precipitate obtained was characterised as Ph₂PCH₂-

CH(COOLi)(CH₂COOLi) (PC). The yield of this synthesis was 46%. ¹H NMR/D₂O: δ (ppm) 2.2 (4H, CH₂); 3.5 (1H, CH); 7.3 (10H, Ph). ³¹P NMR/D₂O: δ (ppm) –20.8. IR/KBr (cm^{–1}): 1580 (COO), 1410 (COO). The acid form of this phosphine has also been analysed: ¹H NMR/CDCl₃: δ (ppm) 2.4–3.2 (5H, CH₂–CH–CH₂), 7.3 (10H, Ph), 9.8 (2H, COOH). ¹³C NMR/CDCl₃: δ (ppm) 28.5 (CH₂), 31.5 (CH₂), 35 (CH), 138.5 (Ph), 140.5 (Ph), 142 (Ph), 174.5 (C(O)), 176 (C(O)).

2.4. Experimental procedure for catalytic reactions

In a typical experiment, 51.6 mg of [Rh(acac)(CO)₂] (0.2 mmol) and 312.2 mg of PNS (0.8 mmol) were dissolved in 20 ml of water. Methyl acrylate (9 ml, 100 mmol) was diluted with 40 ml of toluene. The two

Table 2

Methylacrylate hydroformylation with various water-soluble phosphines at 50 bar of CO/H₂^a

Entry	Phosphine	Phosphine/ rhodium ratio	Toluene/ water ratio ^b	Temperature (°C)	Time (h)	Conversion (mol%)	Aldehyde yield (mol%)	α/β ratio	Methyl propionate yield (mol%)
1	TPPMS	2	4	80	1	100	62	3.7	38
2	PNS	2	4	80	4	100	73	1.8	27
3 ^c	PNS	2	4	80	3	100	57	1.6	43
4 ^d	PNS	2	4	80	5	100	75	2.2	25
5	PNS	2	2	80	6	100	77	2.7	23
6	PNS	2	2	50	21	81	58	14	23
7	TPPMS	4	2	50	8	100	83	63	17
8	PNS	4	2	50	21	100	60	22	40
9	PC	4	2	50	21	100	83	18	17
10 ^e	PC	4	2	50	19	74	68	25	6
11 ^f	PC	4	2	50	21	100	76	22	24
12 ^g	PC	4	2	50	21	100	76	22	24

^a Reaction conditions: Rh(acac)(CO)₂ 0.2 mmol; methylacrylate 100 mmol.^b Toluene and water volumes were 40/10 ml and 40/20 ml, respectively.^c Reaction carried out at pH 7 (addition of H₂SO₄ for neutralisation).^d [RhCl(CO)₂]₂ was used instead of [Rh(acac)(CO)₂].^e 100 mmol of methyl acrylate were added after a first reaction cycle had finished.^f The reaction components were stirred during 1 h at 50°C and 50 atm CO/H₂ before methyl acrylate was introduced to the autoclave.^g The reaction components were stirred during 1 h at 50°C before the pressure at 50 atm was applied.

mixtures were then transferred to the autoclave under dinitrogen. The autoclave was pressurised to 50 bar with CO/H₂ and heated at 50°C until completion of reaction (stirring speed: 800 r.p.m.). At the end of the reaction, the autoclave was cooled and degassed. The organic layer was then analysed by gas liquid chromatography. Products were identified by comparison of GLC retention times and spectral characteristics with authentic samples.

3. Results and discussion

Usually in the hydroformylation of alkyl acrylates, three products are formed: normal (β) and branched (α) aldehydes, and the corresponding propionate as a hydrogenation reaction product (Scheme 1). Reaction selectivities depend on phosphine, temperature and pressure. At high pressure, branched (α) aldehydes are usually main products [28,29].

3.1. Methyl acrylate hydroformylation with [Rh(acac)(CO)₂]/PNS and [Rh(acac)(CO)₂]/PC system

Hydroformylation reaction was studied at 10 and 50 bar (Tables 1 and 2). Results obtained with the [Rh(acac)(CO)₂]/PNS catalytic system in various solvents at 10 bar are summarised in Table 1. In water, hydroformylation of methylacrylate did not occur and the only product observed was methyl propionate (entry 1 in Table 1). In toluene, the yields of α -aldehyde are generally low (6–12%). In THF, α -aldehyde yields are higher than in toluene. The only hydroformylation product under such conditions was α -aldehyde. At two different methyl acrylate concentrations, the conversion was 100%, but only ca. 20% of α -aldehyde was obtained (entries 5 and 6 in Table 1). In the two-phase system water/toluene, the yield of α -aldehyde was similar to those obtained in pure toluene but the activity was lower (entries 3 and 7 in Table 1). A slight increase in PNS/Rh ratio has no influence on the hydroformylation reaction course. However, the reaction yield depends on the acrylate/Rh ratio and the conversion decreases at higher concentration of methyl acrylate (entries 7 and 8 in Table 1).

Consequently, the hydrogenation of methyl acrylate to methylpropionate is the main reaction at 10 bar whatever the solvent used. A comparable significant hydrogenation has also been observed in a typical homogeneous system modified with triphenylphosphine (entry 2 in Table 1). However, high selectivities in hydroformylation products can be achieved by using higher pressures of CO/H₂ (Table 2). Under such conditions, the [Rh(acac)(CO)₂]/PNS catalytic system gives ca. 75% yield of aldehyde at 50 bar CO/H₂ and

the hydrogenation was reduced to ca. 25% (entry 4 in Table 2).

The hydroformylation of methyl acrylate was also studied in the system containing [Rh(acac)(CO)₂] as catalyst precursor and the phosphine PC. The results in Table 2 show that the [Rh(acac)(CO)₂]/PC catalytic system is more active and selective than the [Rh(acac)(CO)₂]/PNS system (compare entries 9–12 with 8 in Table 2). High selectivity is demonstrated by the higher total yield of aldehydes (ca. 80%) as well as by the high α/β ratios, ca. 20. The hydroformylation selectivities obtained with PC or PNS are comparable with those obtained with the well-known water-soluble TPPMS (compare entries 1 and 2 with 7 and 9 in Table 2). However, the activities were lower. These results are probably due to the amphiphilic character of the TPPMS [30]. With this phosphine, the organic layers was yellow–red at the end of the reaction. This colour undoubtedly indicates that significant amounts of rhodium move into the organic phase, which led us to consider that hydroformylation could also occur in the organic layer. In contrast to TPPMS, the organic phase was colourless with PNS and PC. We assume that the hydroformylation occurs only in the aqueous phase with these phosphines. In this case, mass-transfer between aqueous and organic layers plays a more important role and could explain the lower activities.

Some in situ catalyst preparations have been tested to improve the reaction selectivity, especially to decrease hydrogenation and isomerization. In the first experiment, the mixture of catalyst precursor and methyl acrylate was heated during 1 h without CO/H₂ (entry 12 in Table 2). In the second experiment, the catalyst precursor under CO/H₂ but without methyl acrylate was also heated during 1 h (entry 11 in Table 2). However, in both experiments, almost identical selectivity was observed and the contribution of hydrogenation was slightly higher than that in a standard experiment (compare entries 11 and 12 with 9 in Table 2). The best results were obtained when the catalyst was reused. In this case, the α -aldehyde selectivity reached 92% (entry 10 in Table 2). This proves a high catalyst reactivity over 40 h.

3.2. Spectroscopic studies of the catalyst transformation in the system [Rh(acac)(CO)₂]/PNS

In the post-reaction mixture the organic phase was colourless whereas the water phase was intensive red–orange. The water phase contained a mixture of substituted rhodium carbonyls of general formula Rh₄(CO)_{12–x}(PNS)_x identified on the base of IR spectra (ν (CO) 2043, 2003, 1812 cm^{–1}) which are very similar to that of Rh₄(CO)_{12–x}(PPh₃)_x [32]. In some cases, when a higher concentration of methyl acrylate was used, additional small amounts of insoluble [Rh₆(CO)₁₆](IR: ν (CO) 2076, 1800 cm^{–1}) were found.

Spectroscopically monitored transformations of rhodium catalyst precursors under hydroformylation reaction conditions are illustrated in Scheme 3.

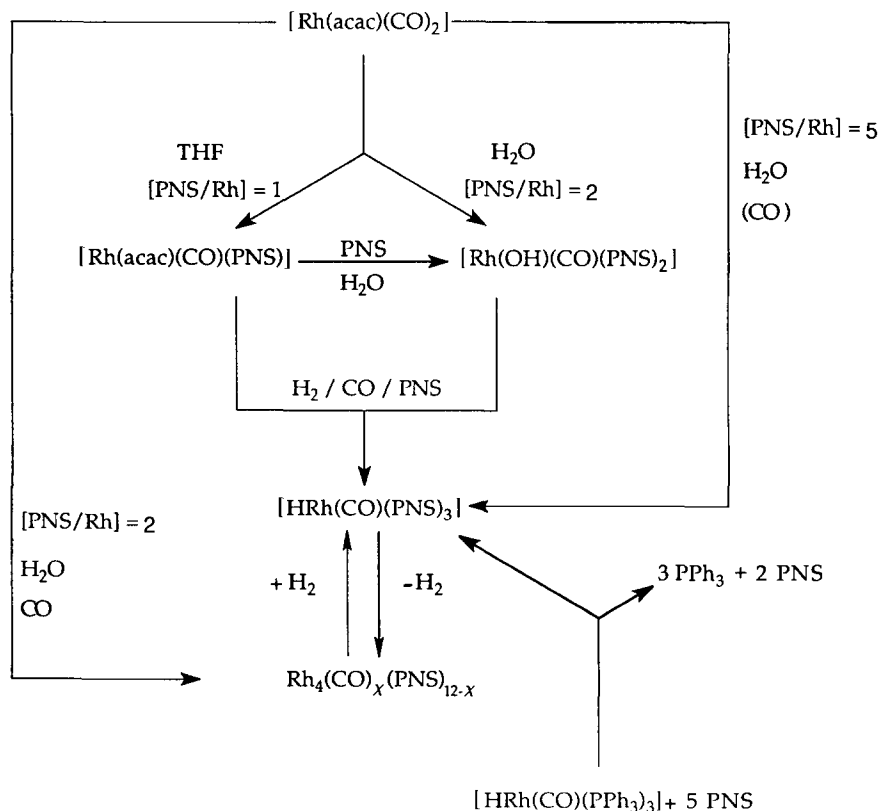
$[\text{Rh}(\text{acac})(\text{CO})(\text{PNS})]$, the precursor of catalytically active form, is the reaction product of $[\text{Rh}(\text{acac})(\text{CO})_2]$ and PNS ($[\text{PNS}]/[\text{Rh}] = 1$) in toluene or THF. It has the following spectroscopic data. IR $\nu(\text{CO})$ 1973 cm^{-1} , ^{31}P NMR (THF) 42.6 ppm $J_{\text{Rh-P}} 173.7$ Hz, ^1H NMR (THF) 1.76 (3H, CH_3 , acac), 2.0 (3H, CH_3 , acac), 5.4 (1H, CH, acac). Similar complexes have been obtained recently with water-soluble phosphines of formula $\text{P}[(\text{CH}_2)_n\text{C}_6\text{H}_4\text{-4-SO}_3\text{Na}]_3$ [15]. Further reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PNS})]$ with an excess of PNS in water leads to elimination of acetylacetonate as Hacac and formation of $[\text{Rh}(\text{OH})(\text{CO})(\text{PNS})_2]$ (IR $\nu(\text{CO})$ 1980 cm^{-1} , ^{31}P NMR 26 ppm $J_{\text{Rh-P}} 124$ Hz). This complex has also been obtained in direct reaction of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with PNS in aqueous or water–toluene solution. Similar hydroxy derivatives of rhodium with TPPTS have already been reported [31].

A mixture of substituted carbonyls $\text{Rh}_4(\text{CO})_{12-x}(\text{PNS})_x$ was obtained as the reaction product of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with PNS ($[\text{PNS}]/[\text{Rh}] = 2$) under 1 atm of CO after 15 h. Their IR characteristics are identical to those recorded for hydroformylation post-reaction mixtures.

At higher PNS concentration ($[\text{PNS}]/[\text{Rh}] = 5$) the reaction in water does not stop at $[\text{Rh}(\text{OH})(\text{CO})(\text{PNS})_2]$, but runs further, producing the hydride complex $[\text{HRh}(\text{CO})(\text{PNS})_3]$. The main characteristics of this new hydride are: IR $\nu(\text{CO})$ 1923 cm^{-1} , $\nu(\text{Rh-H})$ 2003 cm^{-1} , ^{31}P NMR 29.7 ppm, $J_{\text{Rh-P}} 151$ Hz, ^1H NMR -10.5 ppm, q, $J_{\text{P-H}} 18$ Hz, $J_{\text{Rh-H}} 2$ Hz. The presence of three PNS molecules is clearly indicated by the observation of a quartet for the hydride resonance at -10.5 ppm. Furthermore, all the above data are consistent with those reported for the water-soluble hydride rhodium complexes $[\text{HRh}(\text{CO})\{\text{P}[(\text{CH}_2)_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3\}]$ and $[\text{HRh}(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3\}]$ [15,31], and similar to those of $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ [9,31].

The hydride complex $[\text{HRh}(\text{CO})(\text{PNS})_3]$ can be formed from $[\text{Rh}(\text{acac})(\text{CO})_2]$ in water (a source of hydrogen) and in the absence of carbon monoxide. This differed from $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ which was formed from $[\text{Rh}(\text{acac})(\text{CO})_2]$, only in the presence of CO [9,31]. $[\text{HRh}(\text{CO})(\text{PNS})_3]$ could also be prepared independently from $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ via an exchange reaction with a five-fold excess of PNS. The reaction was complete after ca. 30 min (Scheme 3).

The carbonyl complexes in the post-reaction mixtures are probably produced by the decomposition of hydride species containing less than three PNS per



Scheme 3. Transformations of $[\text{Rh}(\text{acac})(\text{CO})_2]$ and $[\text{HRh}(\text{CO})(\text{PPh})_3]$ in the presence of PNS.

rhodium. Formation of carbonyl complexes due to the deficiency of phosphines was also observed in other systems [32].

4. Conclusion

We have demonstrated that the new water-soluble phosphines PNS and PC are suitable for hydroformylation of methylacrylate in a two-phase system. High yields and selectivity of α -aldehyde (ca. 80% with a ratio α/β :20) can be obtained. The use of these new water-soluble phosphines in other transition-metal-catalysed reactions in aqueous-organic two-phase system is being studied.

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