# A New, Efficient, and in Some Cases Highly Regioselective Water-Soluble Polymer Rhodium Catalyst for Olefin Hydroformylation

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**Abstract:** A water-soluble complex Rh/PPA($Na^+$)/DPPEA ***1*** was obtained from poly(4-pentenoic acid) (PPA) and bis[2-(diphenylphosphino)ethyl]amine (DPPEA). Complex ***1*** is a highly active catalyst for the hydroformylation of olefins. Some selectivity for linear aldehydes was observed in the hydroformylation of aliphatic olefins, while high ratios of branched aldehydes resulted in the case of vinyl ethers. Complex ***1*** is also the first polymeric water-soluble metal complex which can catalyze the conversion of vinylarenes to 2-arylpropanals in a highly chemoselective and regioselective manner.

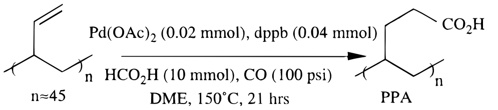
## Introduction

Aqueous organometallic catalysis has recently become a very active field of research.[1] Processes using water as the solvent are environmentally and economically attractive. Indeed, in addition to the ease of catalyst separation from the products, water is environmentally safe and inexpensive.

Water-soluble transition metal complexes have been used as catalysts in several significant commercial processes.[2] For example, the water-soluble catalyst $HRh(CO)(TPPTS)_3$ (TPPTS: trisodium tris(*m*-sulfonatophenyl)phosphine) is used for the hydroformylation of propene.[3] In the case of higher olefins, the hydroformylation reactions are limited by the solubility of the substrate in the aqueous phase where the reaction is presumed to occur.[4] To solve this problem, several approaches have been taken to increase the rate of the hydroformylation reaction by improving the affinities between the two phases. Surfactants[5] and modified cyclodextrins[6] as well as polar solvents such as an alcohol[7] were added in order to enhance the reaction rates. Supported aqueous phase catalysts are effective for the hydroformylation of olefins.[8] The enhancement of the catalytic activity was achieved by the addition of water-soluble organic ligands such as $P(Ph(SO_3))_3$ and inorganic salts which increase the concentration of the catalyst at the interface.[9] Among several new ligands with surfactant structures,[10a−d] surface active phosphines,[10b,c] and poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) (PEVV),[10d] have shown high activities for the hydroformylation of olefins. Recently, new water-soluble phosphine ligands were easily prepared by reaction of diphenylphosphine moieties, with coupling of triphenylphosphine moieties to water-soluble polymers.[11] We report, herein, the synthesis of a new water-soluble polymeric rhodium complex and its application for the hydroformylation of higher olefins especially vinylarenes.

## Results and Discussion

**(1) Synthesis of the Water-Soluble Rhodium Catalyst Rh/PPA($Na^+$)/DPPEA 1.** Poly(4-pentenoic acid) (PPA) (Mw = 4900, Mw/Mn = 2.96) was prepared by the catalytic hydrocarboxylation of 1,2-polybutadiene using $Pd(OAc)_2$/DPPB/HCOOH system (eq 1).[12]



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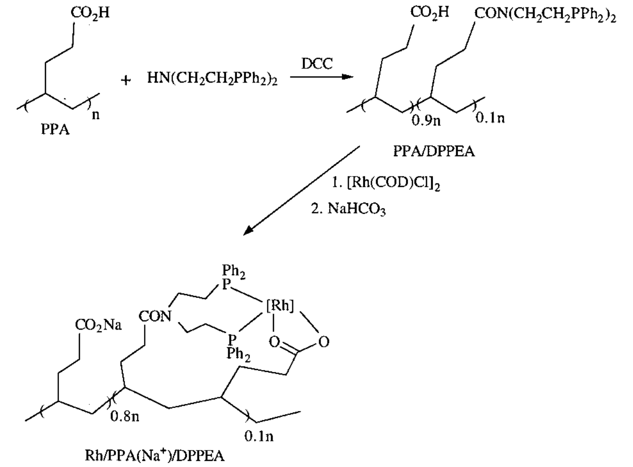
**Scheme 1**



Bis[2-(diphenylphosphino)ethyl]amine (DPPEA)[13] was acylated with PPA using dicyclohexylcarbodiimide (DCC) as the coupling agent in THF. The resulting PPA/DPPEA ligand was characterized by $^{31}$P NMR which shows the presence of two signals at $d = -20.05$ and $-21.10$ ppm. The splitting observed, consistent with occurrence of the acylation reaction ($^{31}$P NMR spectrum of $HCl \cdot NH(CH_2CH_2PPh_2)_2$ shows only one signal at $d = -18$ ppm), is a consequence of slow rotation about the amide bond.[13d] PPA/DPPEA was reacted, in THF, with the rhodium dimer $[Rh(COD)Cl]_2$ to give the polymeric complex Rh/PPA/DPPEA with an average molecular weight of 7712 and a polydispersity of 3.1. After the addition of aqueous $NaHCO_3$ followed by ethyl acetate, the reaction mixture separated into two phases, in which the aqueous phase became yellow while the organic phase changed from yellow to colorless indicating that the rhodium complex was transferred to the aqueous phase. This is further supported by $^{1}$H and $^{31}$P NMR analyses of the organic phase after evaporation, which did not show any traces of phosphine ligand. After evaporation of water to dryness, the water-soluble complex thus obtained (Rh/PPA($Na^+$)/DPPEA; 1 (Scheme 1) was characterized using different techniques.

The $^{31}$P NMR ($D_2O$) spectrum of **1** displays a new broad signal at $d = +20$ ppm (94%) indicating that the complexation reaction occurred. Another small signal was observed at $d = +32$ ppm (6%) and was due to the corresponding phosphine oxide. The broadening of the signals due to the physical properties of this material limits the information (i.e., coupling constants) assignably by this method. The $^{13}$C NMR ($D_2O$) spectrum of **1** did not show any signal characteristic of 1,5-cyclooctadiene. However, it exhibits the signal of the aromatic carbons centered at 130 ppm, the amide signal at 160 ppm, and the carbonyl signals at 180 and 182 ppm. The small signal at 180 ppm is attributed to the carboxylate groups which are, probably, coordinating to the rhodium atom, while the signal at 182 ppm is assigned to the sodium carboxylate groups (the $^{13}$C NMR spectra of the polyacid (PPA) and its sodium salt show the carbonyl signals at 175 and 182 ppm, respectively).

**Table 1.** Hydroformylation of Aliphatic Olefins Using Water-Soluble Rh/PPA($Na^+$)/DPPEA as the Catalyst[a]

| entry | substrate | time (h) | convn % | selectivity[b] % | L/B[c] |
|---|---|---|---|---|---|
| 1 | 1-dodecene | 1.5 | 45 | 40[d] | 2.9 |
| 2 | 1-dodecene | 16 | 100 | 53[d] | 2 |
| 3 | 1-octene | 16 | 100 | 60[e] | 2 |
| 4 | 4-vinylcyclohexene | 4 | 21 | 96 | 5 |
| 5 | *n*-butylvinyl ether | 16 | 25 | >99 | 0.2 |
| 6[f] | phenyl vinyl ether | 16 | 17 | >99 | B only |

[a] Reaction conditions: substrate (10 mmol), Rh/PPA($Na^+$)/DPPEA (50 mg, 0.015 mmol of Rh) in 3 mL of water, $CO/H_2$ (1/1) 600 psi, 90 °C. [b] Selectivity for aldehydes. [c] Molar ratio of linear (L) to branched aldehyde (B) as determined by 1H NMR. [d] The other product was 2-dodecene. [e] The other product was 2-octene [f] The reaction was performed using 2 mmol of phenyl vinyl ether in the presence of Rh/PPA($Na^+$)/DPPEA (10 mg, 0.003 mmol of Rh).

The X-ray photoelectron spectrum for the rhodium in the catalyst **1** shows a well-resolved spin doublet with binding energies Rh 3d$_{3/2}$ and Rh 3d$_{5/2}$ at 313.5 and 308.5 eV, respectively. The full width at half-maximum (fwhm) of Rh 3d$_{5/2}$ is $\Delta_{1/2} = 3$ eV. These values, in agreement with the ESCA data for Rh(I) supported catalysts,[14] show that the rhodium in the catalyst **1** is in the monovalent state.

The phosphorus content was determined by elemental analysis and corresponded to 1.8% (0.58 mmol of phosphorus per gram of **1**), while absorption atomic spectroscopy (AAS) gave the rhodium content as 3.19% (0.3 mmol of rhodium per gram of **1**) (P/Rh = 1.93).

**(2) Hydroformylation of Olefins Catalyzed by Rh/PPA-($Na^+$)/DPPEA 1.** The hydroformylation of neat 1-dodecene catalyzed by the water-soluble complex **1** at 90 °C under 600 psi of $CO/H_2$ ($CO/H_2 = 1/1$) for 1.5 h resulted in 45% conversion of the substrate and 40% selectivity for hydroformylation with a 2.9/1.0 ratio of linear to branched aldehyde (Table 1, entry 1) and a turnover frequency of 80 mol/mol(Rh)/h. These data indicate that **1** is as active and selective as the water-soluble complex Rh/PEVV.[10d] The increase of reaction time to 16 h led to full conversion and 53% selectivity for the aldehydes with L/B = 2 (Table 1, entry 2). The catalyst gave the same activity and selectivity for three cycles, and the analysis of the organic phase by atomic absorption indicated that no rhodium was leached from the aqueous to the organic phase. The hydroformylation of 1-octene, under the same conditions, afforded similar results (Table 1, entry 3), while 4-vinylcyclohexene gave the aldehydes in 21% conversion and 96% selectivity with L/B ratio of 5 (Table 1, entry 4), the internal double bond being inert. Branched aldehydes were obtained as the major or only product in the case of vinyl ethers. While *n*-butyl vinyl ether gave the aldehydes in 25% conversion and a B/L molar ratio of 5, only the branched aldehyde was formed in the case of phenyl vinyl ether although the conversion of the substrate was low (Table 1, entries 5 and 6). The increase of reaction time or the amount of the catalyst, in the case of phenyl vinyl ether, resulted in the decomposition and polymerization of the substrate, and no improvement in the yield of 2-phenoxypropanal was observed.

When styrene was hydroformylated under the same conditions as for 1-dodecene (except the reaction temperature was 70 °C), aldehydes were obtained in 98% selectivity with 13% conversion of styrene after 2 h, 2-phenylpropanal being the major aldehyde (B/L = 93/7) (Table 2, entry 1). The increase of the reaction time to 16 h led to full conversion of starting material with B/L = 95/5 (Table 2, entry 2). This interesting result proves that the water-soluble catalyst Rh/PPA($Na^+$)/DPPEA is more active and much more regioselective than the water-soluble system Rh−PEVV which gave very low conversion of styrene[10d] and $Rh(acac)(CO)_2$/TPPTS or $Rh(acac)(CO)_2/PR[(CH_2)_8C_6H_4$-

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**Table 2.** Hydroformylation of Vinyl Arenes Using Water-Soluble Rh/PPA($Na^+$)/DPPEA as the Catalyst[a]

| entry | substrate | time (h) | convn % | selectivity[b] % | isolated yields % | B/L[c] |
|---|---|---|---|---|---|---|
| 1 | styrene | 2 | 13 | 98 | | 93/7 |
| 2 | styrene | 16 | 100 | 98 | 98 | 95/5 |
| 3 | *p*-methoxystyrene | 24 | 100 | 97 | 94 | 88/12 |
| 4 | *p*-methylstyrene | 24 | 100 | 98 | 96 | 92/8 |
| 5 | *p*-bromostyrene | 24 | 100 | >99 | 99 | 95/5 |
| 6 | *p*-fluorostyrene | 24 | 100 | >99 | 98 | 94/6 |
| 7[d] | 2-vinylnaphthalene | 24 | 100 | >99 | 98 | 96/4 |

[a] Reaction conditions: substrate (10 mmol), Rh/PPA($Na^+$)/DPPEA (50 mg, 0.015 mmol of Rh) in 3 mL of water, CO/H (1/1) 600 psi, 70 °C. [b] Selectivity for aldehydes. [c] Molar ratio of branched (B) to linear aldehyde (L) as determined by $^1H$ NMR. [d] THF (3 mL) was added in order to dissolve 2-vinylnaphthalene.

*p*-$SO_3Na]_2$, which afforded the products in B/L ratios ranging from 66/34 to 73/27.[10b] This system is also more active and appreciably more regiselective than the supported aqueous phase catalyst[8e] and shows comparable regioselectivity with some homogeneous systems such as Rh(cod)($\eta^6$-$PhBPh_3$)[15] and [Rh-(NBD)(L−L)]$BF_4$ where L−L is 1,2-bis[bis(pentafluorophenyl)-phosphino]ethane.[16] The generality of Rh/PPA($Na^+$)/DPPEA activity and regioselectivity was tested using a variety of substituted styrenes and 2-vinylnaphthalene (Table 2, entries 3−7). These results demonstrate the high activity of the catalyst (full conversion in all the cases after 24 h) and excellent regioselectivity with B/L ratios which range from 92/8 to 96/4, except in the case of *p*-methoxystyrene where B/L = 88/12. To our knowledge, this is the first highly active polymeric water-soluble catalyst which convertes vinylarenes to the corresponding 2-arylpropanals in a highly regioselective manner.

## Conclusions

The water-soluble complex Rh/PPA($Na^+$)/DPPEA is a new, highly active catalyst for the hydroformylation of olefins and constitutes the first polymeric water-soluble catalyst leading to 2-arylpropanals in a highly regioselective manner.

## Experimental Section

**Materials.** All olefins were purchased from Aldrich Chemical Co. and used without further purification.

$[Rh(COD)Cl]_2$ was prepared according to the literature method.[17]

Solvents were dried and distilled prior to use by known methods.

**Instruments.** IR spectra were recorded using a Bomem MB100−C15 (FT-IR) instrument. $^1H$, $^{31}P$, and $^{13}C$ NMR spectral determinations were made on either a Varian Gemini 200 or Bruker 500 MHz spectrometer using $D_2O$ and $CDCl_3$ as the solvents. Phosphorus chemical shifts are relative to external 85% $H_3PO_4$.

The rhodium content of the catalysts was obtained by atomic absorption spectroscopy (AAS), using a Varian Spectr. Plus 250.

X-ray photoelectron spectroscopy (XPS) measurements were obtained using Phi 5500 system instrument with MgKa radiation (1253.6 eV). The binding energies for Rh were referenced to carbon (1s = 284.5 eV).

Molecular weights and molecular weight distributions were measured at 45 °C by gel permeation chromatography (Waters high-pressure instrument Model 510 pump), using a series of 10 microns particle size $\mu$.Styragel Columns HT 3, HT 4, and HT 5 with the effective molecular weight ranges of 500−30 000; 5 000−600 000; and 50 000 to $4 \times 10^6$, respectively, and a differential refractometer (Model 410). Tetrahydrofuran was used as eluant at a flow rate of 1 mL/min, and a sample concentration of 1 mg/mL was used. Polybutadiene narrow standards were used for calibration.

**Synthesis of Rh/PPA($Na^+$)/DPPEA, 1. Preparation of Bis[(2-diphenylphosphino)ethyl]amine.** Bis[(2-diphenylphosphino)ethyl]-amine was prepared from bis(2-chloroethyl)amine using a literature method.[13a] The compound was purified as an air-stable hydrochloride after recrystallization from acetonitrile.[13c,d] Before the acylation reaction, the amine hydrochloride was dissolved in degassed methylene chloride and then treated with a degassed aqueous solution containing a stoichiometric amount of sodium hydroxide. The organic phase was dried ($MgSO_4$) and then evaporated to yield the free amine which was kept under nitrogen.

**Preparation of Rh/PPA($Na^+$)/DPPEA.** To a solution of polyacid (PPA) (2 g, equivalent to 20 mmol of $CO_2H$ groups) in dry THF (50 mL) was added 1,3-dicyclohexylcarbodiimide (DCC) (577 mg, 2.8 mmol) and then a solution of $HN(CH_2CH_2PPh_2)_2$ (884 mg, 2 mmol) in dry THF (20 mL) ($N_2$ atm). The reaction mixture was stirred at room temperature for 24 h, the volume of the mixture was then reduced to 20 mL (rotary evaporation), and dicyclohexylurea (DHU) was precipitated and removed by filtration under nitrogen. The filtrate was then evaporated affording the phosphinated polyacid (PPA/DPPEA) which was analyzed by $^{31}P$ NMR. PPA/DPPEA ligand was dissolved in THF (50 mL) under $N_2$ and a solution of freshly[16] prepared $[Rh(COD)Cl]_2$ (493 mg, 1 mmol), in THF (20 mL) was added by syringe. The yellow solution was stirred at room temperature for 24 h. An aqueous degassed solution of $NaHCO_3$ (1.5 g, 18 mmol) was added followed by ethyl acetate (50 mL). After 30 min, the mixture consisted of a yellow aqueous solution and colorless organic phase. The former phase was evaporated to dryness to give the water-soluble rhodium complex (Rh/PPA($Na^+$)/DPPEA, **1**) as a yellow powder. The organic phase was also evaporated and analyzed by $^1H$ and $^{31}P$ NMR which did not show any traces of phosphine ligand.

**Catalytic Hydroformylation Procedure.** In a 45 mL autoclave equipped with a glass liner containing a stirring bar was placed an aqueous solution of Rh/PPA($Na^+$)/DPPEA (10−50 mg, 0.003−0.015 mmol of Rh) and the olefin (2−10 mmol) (in the case of 2-vinylnaphthalene, 3 mL of THF were added to dissolve the substrate). The autoclave was flushed three times with carbon monoxide and pressurized to 400 psi, and then hydrogen was introduced up to a total pressure of 600 psi. The reactor was then placed in an oil bath at the desired reaction temperature for the required reaction time (see Tables 1 and 2). The autoclave was cooled to room temperature, excess CO/$H_2$ was released, and the organic phase was separated from the aqueous phase, diluted with diethyl ether, dried ($MgSO_4$), and then analyzed by $^1H$ NMR spectroscopy after the solvent was evaporated. The isolated yields were obtained after purification by silica gel chromatography using 9/1 petroleum ether/ethyl acetate as the eluant (under $N_2$) and then analyzed by NMR.

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