

Polyether phosphite for hydroformylation of higher olefins in non-aqueous system and catalyst recovery

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Abstract

A new rhodium catalyst recycling system for non-aqueous hydroformylation of 1-decene is described using a polyether phosphite, OPGPP with a polyether chain of over 19 ethylene glycol units. The corresponding rhodium complexes formed in situ are active for non-aqueous hydroformylation of 1-decene. The catalysts precipitated from the reaction mixture on cooling to room temperature or lower and were reused up to six times without obvious decrease in activity. P loss in the seventh reaction run was detected to be 0.92%. Complex OPGPP/Ru₃(CO)₃ formed in situ has also been proved to be a moderate catalyst for the non-aqueous hydroformylation of 1-decene. The catalysts retained considerable activity up to 87.1% after four successive reaction runs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphite; Rhodium; Hydroformylation; Catalyst separation

1. Introduction

Considerable attention has been paid to aqueous/organic biphasic catalysis in the benign, economic chemical process, which has been regarded as a royal road to surpass catalyst-product separation and catalyst recycling [1–3]. However, limitations of water as solvent were inevitably confined such as in a system with water sensitive catalyst or substrates, at the same time, existence of water as solvent decreases regioselectivity for asymmetric catalysis compared to non-aqueous homogeneous catalysis. New reaction mediums avoiding water as solvent, such as perfluorinated hydrocarbons and ionized solvents have been new focal points [4–7]. However, it is questionable whether the recently announced FBS and NAILs would achieve a breakthrough in larger scale industry, because of the toxicity of the perfluorinated hydrocarbons and the corresponding perfluorinated phosphines as ligands and requirement of strict purity for the ionized solvents, respectively. The much higher price of these special solvents than normal

solvents, especially water, methanol etc., has also to be considered in practical industry.

Another approach to facilitate catalyst-product separation has long been attached for the catalyst to a polymeric, organic (e.g. polystyrene, dendrimers) or inorganic (e.g. polysiloxanes) resin [8–10]. Nevertheless, activity decrease suffering from diffusion of catalyst in solvent was often encountered and catalyst leaching remained a problem for industrial application. Recently, transition-metal catalysts with soluble supports were highlighted in literature due to the characteristic advantage of one-phase catalysis and easy separation of the catalysts from the mixture by various procedures [11–13]. Polyethylene glycol (PEG) derivatives have long found their application in combinational synthesis such as synthesis and purification of peptide and zymes. Previously we reported some polyether-derived triphenylphosphine ligands and their application in aqueous/organic biphasic hydroformylation of higher olefins [14–17]. It has been recently observed that these polyether phosphines are slightly soluble in some apolar solvents such as toluene and heptane at room temperature, providing a good approach to meet simple catalyst separation and recovery after reaction.

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The use of phosphite in the rhodium catalyzed hydroformylation has received much attention because of its great improvement in activity compared to the generally employed triphenyl phosphine (TPP), especially obvious for the long linear olefins and less active internal olefins [18–20]. Separation of catalyst from products in industry is mainly done through distillation, which requires strict thermal conditions and inevitably increases the byproducts. The higher temperature required for separation of hydroformylation products of higher olefin causes worse decomposition of the modified complexes and some phosphites, eventually inducing worse leaching of catalyst.

We previously reported a novel polyether phosphite (OPGPP) to facilitate aqueous two-phase hydroformylation of water-immiscible higher olefins and styrene, but there was a considerable loss in activity after four successive reaction runs owing to the hydrolysis of the phosphite in water [21,22]. In this paper, we suggest polyether phosphite OPGPP for the hydroformylation of higher olefins in the absence of water. It was observed that the catalyst precipitated quantitatively from the reaction mixture on cooling to room temperature or lower temperature. The catalyst was easily recovered by simple decantation after reaction.

2. Results and discussion

2.1. Solubility of phosphines in organic solvents

2.1.1. Solubility of polyether phosphines in solvents at room temperature

As was demonstrated in literature, poly(ethylene glycols) (PEGs) and their derivatives with weight of 1500–6800 can be quantitatively precipitated from benzene, acetone, methanol, or methylene chloride by addition of heptane, ethyl ether, or sometimes by cooling to low temperature [23,24]. These properties combined with their easy functionalization offer a possibility of designing various soluble but recoverable materials such as catalysts and synthetic intermediates [23,24]. At room temperature, the PEGs in the weight range from 1500 to 6800 have only a slight solubility of less than 0.1% in heptane, implying that catalyst with them as support will be better recovered after the reaction. Comparing the structure and weight of OPGPP with that of the corresponding PEGs, OPGPPs do not suffer from changes in physical characters such as solubility in solvents. In view of recovery of catalysts with PEG as support, longer PEGs benefit in facilitating catalyst separation. In addition, PEGs precipitate in cooled toluene or ethanol while they dissolve in hot solvents. This provides an approach to prepare thermally separable catalyst in homogeneous catalysis.

OPGPPs with different glycol units possess different solubility in ambient toluene, heptane and other solvents. The results are summarized in Table 1.

As is indicated in Table 1, OPGPPs derived from PEG-R dissolve in polar solvents such as CH_2Cl_2 and THF at room temperature. Lower OPGPP with 600 weight has considerable solubility in toluene, while it is insoluble in heptane at room temperature. With increasing weight of OPGPP, it has decreasing solubility in apolar solvents such as heptane. When n is equal to 58, OPGPP has a slight solubility of $0.3250 \mu\text{g P}$ in 100 ml heptane, indicating very slight (0.045%) loss of phosphite in solvent. From the viewpoint of catalyst recovery, higher OPGPP and apolar solvents such as heptane are preferred for non-aqueous homogeneous catalysis.

2.1.2. Solubility of OPGPP at different temperature

OPGPPs exist as a liquid at temperatures above 40°C , which means that two liquid phases coexist with OPGPPs as one of them, since only a very small amount of OPGPPs dissolve in some solvents even at higher temperature. From Fig. 1, no more than 3.33% of OPGPP ($n = 58$) dissolves in heptane at 90°C at which phosphite for hydroformylation of higher olefins is usually employed. The sudden increase in phosphorus solubility around 70°C may be ascribed to the existence of critical solubility temperature (CST) [25,26] in this system. This work is in progress.

2.2. OPGPP/Rh catalyzed hydroformylation of higher olefins

Previously we reported the hydrolysis of OPGPP in aqueous two-phase catalysis, in which considerable loss of catalyst was observed in the recycling runs. This may be avoided by using non-aqueous catalytic system. Solubility of OPGPP from Table 1 demonstrates that the least catalyst loss in apolar solvents such as heptane occurs when higher OPGPPs are employed as ligands. In this work, OPGPP with 58 glycol units was taken as ligand for non-aqueous hydroformylation of higher olefins. To compare the results properly, data obtained at the same reaction time are presented. After reaction, the catalysts formed in situ are rose viscous fluid or wax at lower temperature or room temperature.

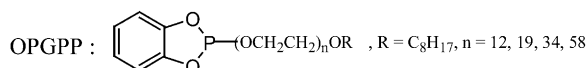
2.2.1. Effect of reaction temperature

It is known that an increasing reaction temperature induced an enhancement in reaction rate. 80% conversion of 1-decene was obtained at 70°C , more than two times that obtained at 60°C (see Table 2). TOF reaches up to 250 h^{-1} at 90°C . In general, less than 2.0 *n*/iso aldehyde ratio was achieved with a 42–60% of linear aldehyde at 60 – 100°C . No hydrogenation product of aldehyde was detected in the reaction mixtures.

Table 1
Solubility of OPGPP^a in heptane and toluene at ambient temperature^b

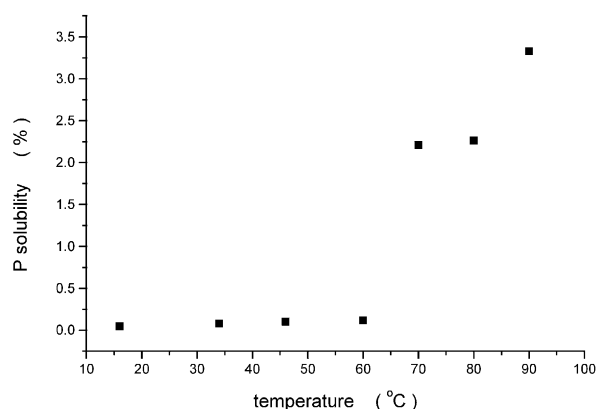
Polyether chain length of OPGPP (<i>n</i>)	Solvent	Temperature (°C)	Solubility (μg P ml ⁻¹ solvent)	Ligand solubility in solvent ^c (%)
12	Heptane	16	154.5000	14.72
12	Toluene	16	/	Fully soluble
19	Heptane	16	42.4100	5.55
19	Toluene	16	/	Largely soluble
34	Heptane	16	9.0375	Partly soluble
58	Heptane	16	0.3250	0.045
58	Toluene	16	171.7625	27.35
58	CH ₂ Cl ₂	16	/	Fully soluble
58	THF	16	/	Fully soluble

^a



^b 2.054 × 10⁻⁴ mol OPGPP/6.0 ml organic solvent.

^c Ligand solubility: P content in solvent/total P addition.



P solubility (%) = Solubility of OPGPP / total OPGPP (based on P content)

Fig. 1. Solubility of OPGPP (*n* = 58) at different temperatures.

2.2.2. Effect of solvents

From Table 3, use of toluene, 1,4-dioxane, anisol, and heptane as solvents promotes almost full conversion of substrate after 4 h. Nevertheless, it was observed that

the color of the reaction mixture with toluene, 1,4-dioxane, anisol, turned out to be somewhat yellow, indicating obvious loss of catalyst in the reaction mixture. In comparison, reaction mixture is colorless in heptane. 4 h were needed to reach up to 98% or so conversion in heptane, while 3 h was enough for toluene, 1,4-dioxane and anisol. This difference may be the result of different solubility of phosphines in various solvents under the reaction conditions. It can be observed that OPGPP dissolves fully in toluene and anisol at temperatures above 50 °C, while just quantitative OPGPP dissolves in heptane even at 80 °C (Fig. 1). Interestingly, it was observed that OPGPP dissolves fully in heptane with accumulation of some quantitative amount of aldehydes. So we assume that the reaction takes place in toluene in homogeneous catalysis. However, with heptane as solvent, homogeneous catalysis and heterogeneous catalysis take place in competition in the early stage of the reaction and when product aldehydes accumulate up to some amount, the reaction becomes homogeneous.

Table 2
Effect of temperature on the reaction

Temperature (°C)	Conversion (%)	Aldehyde yield (%)	<i>n</i> -Undecanal content (%) ^a	Aldehyde <i>n</i> / <i>iso</i>
60	31.4	25.2	60.0	1.50
70	80.0	77.7	56.7	1.31
80	95.1	94.2	51.0	1.04
90	99.4	97.6	48.5	0.94
100	99.7	95.3	42.0	0.72

Reaction conditions: 1-decene 2.0 ml, heptane 4.0 ml, internal standard 0.3 ml, Rh(acac)(CO)₂ 1.058 × 10⁻⁵ mol, OPGPP/Rh = 13, P(CO)/P(H₂) = 1:1, Syngas pressure 5.0 MPa, reaction time 4 h.

^a *n*-Undecanal content = *n*-undecanal/total aldehyde.

Table 3
Hydroformylation in different organic solvents

Solvent	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	Aldehyde <i>n/i</i>
Toluene	3	97.3	95.6	0.92
1,4-Dioxane	3	98.7	97.2	0.93
<i>n</i> -Butyl ether	3	75.0	74.3	0.98
Anisole	3	98.0	97.2	0.93
Cyclohexane	4	98.7	95.4	0.92
Heptane	3	86.4	86.4	1.21
Heptane	4	99.4	97.6	0.94

Reaction conditions: 1-decene 2.0 ml, solvent 4.0 ml, internal standard 0.3 ml, Rh(acac)(CO)₂ 1.058 × 10⁻⁵ mol, OPGPP/Rh = 13, P(CO)/P(H₂) = 1:1, 90 °C, Syngas pressure 5.0 MPa.

2.2.3. Effect of phosphine/rhodium ratio

Table 4 summarized the results from varying the phosphine/Rh ratio and addition of TPP. All results remained similar as the phosphite/Rh ratio was in the range of 13–30. Lower phosphite/Rh ratio below 13 decreased the conversion and caused a clear loss of catalyst evidenced by the color of the mixture. Colorless mixture was obtained with a phosphite/Rh ratio of more than 13. Addition of TPP caused a slight increase in *n/i* ratio of aldehydes from 0.94 to 2.3. Meanwhile, addition of TPP to the reaction system induced a slightly yellow solution.

2.3. Comparison of some polyether phosphine/Rh catalyzed non-aqueous hydroformylation of 1-decene

We also studied the effects of some different polyether phosphines on the hydroformylation and catalyst separation. The comparison was summarized in Table 5.

From Table 5, phosphine A-H/Rh catalysts show considerable activity for the non-aqueous hydroformylation of 1-decene with heptane as solvent, while OPGPP/Rh catalyzed the reaction with the highest conversion. Therefore, a conversion of 99.4% 1-decene and yield of 97.6% aldehydes were obtained in 4 h with OPGPP (*n* = 58)/Rh as catalyst formed in situ from Rh(acac)(CO)₂ with OPGPP (*n* equal to 58) (*P* = 5.0 MPa, *T* = 90.0 °C). In view of catalyst separation, A, B,

E, and H ligands and their rhodium complexes precipitated as a separate phase from heptane after reaction at room temperature. Catalyst separation could be reached by simple decantation.

2.4. Catalyst recycling

The separated catalyst by simple decantation was employed in the successive reaction runs. Results of the catalyst recycling were shown in Table 6. Loss of phosphite in organic phase was determined by ICP technique.

After reaction, the catalyst precipitated as rose viscous wax or mash from the reaction mixture on cooling to room temperature. The separated catalyst was reused up to six times without apparent decrease in activity. Compared with phosphite/Rh catalysts usually separated by distillation in industrial practice, the polyether phosphite modified catalyst possesses an obvious advantage in separation from the product after reaction. Analysis of phosphite in product phase indicated that P loss in reaction mixture after first reaction and second reaction was 7.8 and 7.2% of the original total P, respectively. In more reaction runs, loss of P in the reaction mixture decreased. Loss of P in the seventh reaction run was detected to be only 0.92% of the original total P. This gradual decreasing loss of P in organic phase may be induced by the weight distribution

Table 4
Effect of OPGPP/Rh (mol) ratio and triphenylphosphine on the reaction

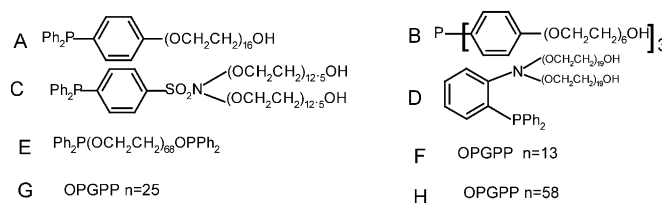
OPGPP/Rh (mol)	PPh ₃ /Rh	1-Decene conversion (%)	Aldehyde yield (%)	Aldehyde <i>n/i</i> so
3		75.3	73.5	0.94
7		90.0	88.3	0.96
13		99.4	97.6	0.94
20		99.7	98.5	0.98
30		99.7	98.9	0.99
3	3	54.3	53.2	0.98
13	4	94.0	93.1	1.3
13	13	95.5	94.6	1.8
13	4.	93.8	93.8	2.3

Reaction conditions: 1-decene 2.0 ml, heptane 4.0 ml, internal standard 0.3 ml, Rh(acac)(CO)₂ 1.058 × 10⁻⁵ mol, P(CO)/P(H₂) = 1:1, 90 °C, Syngas pressure 5.0 MPa, reaction time 4 h.

Table 5
Hydroformylation catalyzed by polyether phosphines/Rh catalyst in the absence of water

TRPTC ligand	Conversion (%)	Aldehyde yield (%)	Catalyst separation (by precipitation)
A	56.7	56.3	Clear
B	31.3	31.3	Clear
C	74.3	73.1	Turbid
D	67.3	63.2	Turbid
E	78.6	78.6	Clear
F	99.7	97.1	Turbid
G	99.5	96.9	Turbid
H	99.4	97.6	Clear

Reaction conditions: 1-decene 2.0 ml, heptane 4.0 ml, internal standard 0.3 ml, Rh(acac)(CO)₂ 1.058 × 10⁻⁵ mol, Ligand/Rh = 13, P(CO)/P(H₂) = 1:1, 90 °C, Syngas pressure 5.0 MPa, reaction time 4 h.



of the polyether group in the molecule. As a general rule, polyether derivatives are mixtures of different weight compounds, in which weight distribution is in accordance with Poisson distribution. As elucidated in Table 1, lower weight phosphites have higher solubility in solvent than higher phosphites as far as OPGPP is concerned. With successive dissolution of lower phosphites in the reaction mixture, higher phosphite retained to be lost in later reaction runs. After several reaction runs, loss of P decreased to some extent since higher phosphites have a slight solubility in heptane. Hence,

although total P-loss from the first run to the seventh run is somewhat too large from a practical viewpoint, this polyether phosphite OPGPP demonstrated its merits for its easy synthesis with low price. P recovery can be improved via pretreatment with solvent before use. It also made sense that decantation on cooling temperature will facilitate the catalyst separation and benefit the recovery of the phosphites and the catalysts.

In comparison, only 71.4% of conversions were obtained in the third reaction run in aqueous–organic biphasic system. The reason for the decrease in activity

Table 6
Recycling of OPGPP (*n* = 58)/Rh catalyst in the single organic phase reaction system and aqueous–organic biphasic reaction system

Reaction runs	Conversion (%)	Aldehyde yield (%)	Aldehyde <i>n</i> / <i>iso</i>	P content in product phase (μg ml ⁻¹)	P loss in product ^c (%)
<i>One phase</i> ^a					
1	99.4	97.6	0.91	60.4350	7.8
2	99.3	97.8	0.95	55.2800	7.2
3	99.2	95.0	0.95	23.3150	3.05
4	96.3	93.0	0.92	18.6350	2.4
5	97.3	96.3	0.93	17.0000	2.22
6	94.3	90.5	0.97	15.1350	1.98
7	93.0	92.4	0.93	7.0650	0.92
<i>Two-phase</i> ^b					
1	99.5	97.0	0.95		
2	91.3	91.3	0.95		
3	83.7	83.7	0.96		
4	71.4	71.4	0.94		

^a Reaction conditions: 1-decene 2.0 ml, heptane 4.0 ml, internal standard 0.3 ml, Rh(acac)(CO)₂ 1.058 × 10⁻⁵ mol, OPGPP/Rh = 13, P(CO)/P(H₂) = 1:1, 90 °C, Syngas pressure 5.0 MPa, reaction time 4 h.

^b *V*_{org}/*V*_{water} = 1/1, other conditions are the same as ^a.

^c Loss of ligand/employed ligand (based on P content).

after three reaction runs may be attributed to the partial hydrolysis of the phosphite in the presence of water as solvent [14,21,22].

2.5. OPGPP/Rh catalyzed hydroformylation of higher olefins in single organic phase system

The above non-aqueous reaction system has also been applied in the hydroformylation of other higher olefins (1-hexene, 1-octene, 1-dodecene, 1-tetradecene) (shown in Table 7). Under the same conditions, more than 95% of conversions were obtained.

2.6. OPGPP/Ru₃(CO)₁₂ catalyzed hydroformylation of 1-decene

Ruthenium complexes have received relatively little attention in the hydroformylation because of their much lower activity than rhodium and cobalt complexes and inevitable hydrogenation of alkenes and aldehydes caused by the former. However, when ruthenium complexes as a cluster consist of several metal atoms, activation of the substrates may take place at more than one metal atom and this can have a profound effect on the activity. Here we directed our attention to use of OPGPP/Ru₃(CO)₁₂ catalyst formed in situ to non-aqueous hydroformylation of 1-decene with heptane as solvent.

In comparison, the above phosphite/Ru₃(CO)₁₂ complex demonstrated similar activity and selectivity with arylphosphite/Ru₃(CO)₁₂ previously reported by Wilkinson [27] (see Table 8). Under the moderate conditions ($T = 130\text{ }^{\circ}\text{C}$, $P = 5.0\text{ MPa}$), a conversion as high as 96.3% with 70.0% of aldehydes yield is obtainable. From the results, considerable hydrogenation of aldehydes to alcohols was determined. Nevertheless, no apparent hydrogenation of 1-decene was detected in the hydroformylation products. After the reaction, the catalysts precipitated as yellow wax from the reaction mixture and could be reused in the successive three runs, retaining considerable activity.

Table 7
Hydroformylation of higher olefins catalyzed by OPGPP/Rh in the single organic phase system

Alkene	Conversion (%)	Aldehyde yield (%)	Aldehyde <i>n</i> / <i>iso</i>
1-Hexene	99.7	96.5	2.30
1-Octene	99.2	96.0	1.45
1-Decene	99.4	97.6	0.91
1-Dodecene	97.3	96.3	0.89
1-Tetradecene	94.5	90.5	0.85

Reaction conditions: olefin 2.0 ml, heptane 4.0 ml, internal standard 0.3 ml, olefin/Rh(acac)(CO)₂ (mol) = 1000, OPGPP/Rh = 13, P(CO)/P(H₂) = 1:1, 90 °C, Syngas pressure 5.0 MPa, reaction time 4 h.

Table 8
OPGPP ($n = 58$)/Ru₃(CO)₁₂ catalyzed hydroformylation and recovery of the catalyst

Reaction runs	Conversion (%)	Aldehyde yield (%)	Alcohol (%)
1	96.3	70.0	25.0
2	95.4	68.3	26.0
3	89.0	63.7	23.1
4	87.1	64.5	22.0

Reaction conditions: 1-decene 1.0 ml, heptane 2.0 ml, internal standard 0.3 ml, Ru₃(CO)₁₂ 0.0072 g, OPGPP 0.64 g, P(CO)/P(H₂) = 1:1, Syngas pressure 5.0 MPa, reaction temperature 130 °C, 9 h.

3. Conclusion

Polyether phosphites OPGPPs with over 19 ethylene glycol units have slight solubility in apolar solvent such as heptane. Accordingly polyether phosphite was employed as ligand in the rhodium catalyzed non-aqueous hydroformylation of 1-decene with heptane as solvent in direction to catalyst separation. The catalysts have shown high activity and selectivity to aldehydes. In contrast to previous rhodium complexes modified by phosphites, the catalysts precipitated from the reaction mixture after reaction on cooling to room temperature or lower. The separated catalyst by simple decantation was reused up to six times without clear decrease in activity. Complexes OPGPP/Ru₃(CO)₃ formed in situ also proved to be a moderate catalyst in the hydroformylation of 1-decene in the absence of water. The catalysts retained considerable activity in the successive reaction runs. Hence an effective non-aqueous catalytic reaction system with polyether phosphites OPGPP has been proposed in the paper. Application of this reaction system to other water-sensitive reaction is anticipated in our further research.

4. Experimental

4.1. General methods

The preparation and purification of materials were performed under prepurified nitrogen using standard Schlenk-type techniques. OPGPP was prepared according to literature [21,22]. Rh(acac)(CO)₂ was from Beijing Chemical Institute and 1-decene from Fluka; toluene, heptane, THF, and ether were distilled from sodium benzophenone ketyl; methylene chloride was distilled from CaH₂. Octanol was treated with sodium and distilled under prepurified nitrogen.

Infrared spectra were recorded on Perkin–Elmer 2000. ¹H- and ³¹P-NMR were recorded at 300, 90 MHz, respectively, on a Varian VXR-300s spectrometer. Chemical shifts are reported in ppm and referenced to

residual deuterated solvent signals for $^1\text{H-NMR}$ and external $85\%\text{H}_3\text{PO}_4$ ($\delta = 0.00$) for $^{31}\text{P-NMR}$. Gas chromatography analysis was run on SP-09 instrument (OV-101) (50 m capillary column, carrier gas: 2.0 atm N_2 , FID detector) equipped with a Shimadzu integrator. Dodecane was used as an internal standard. Mass spectra were measured on a Finnagant 312/SS 200 GC-Mass spectrometer.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES): PLASMA-SPEC-I echelle style element scan Inductively Coupled Plasma-Atomic Emission Spectroscopy (LEEMAN LABS Company). Measured wavelength: 369.24 nm (Rh); order: 61; signal/background ratio: 350; coolant gas (Ar): 12 l min^{-1} ; integration time: 3 s; detection limit: $10\text{--}0.02\ \mu\text{g ml}^{-1}$ (P).

4.2. Preparation of $\text{Ru}_3(\text{CO})_{12}$ [28]

3 g (11.46mmol) $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 120 ml anhydrous MeOH were added to 200 ml standard stainless autoclave with magnetic stirrer. The system was sealed and charged three times with 2.0 MPa CO and pressurized to 5.0 MPa. The autoclave was placed in a thermostatic oil bath with vigorous stirring for 8 h at $125\ ^\circ\text{C}$. On cooling to room temperature, orange needle precipitated from reaction mixture to be filtered. The filtrate was recrystallized in toluene. Yield: 54%. IR analysis: $\nu(\text{CO}) = 2053, 2017, 1998\ \text{cm}^{-1}$.

4.3. Solubility of phosphine in organic solvents by ICP-AES

Standard concentration data of phosphorus containing solution was determined by ICP-AES prior to measuring the concentration of the samples. Exact 1.0 ml of the sample solution was transferred to pre-purified erlenmeyer flask. Solvent was carefully removed by gentle heating. Then 5.0 ml concentrated HNO_3 (65%) was added and the solution was heated to $120\ ^\circ\text{C}$ for 6 h. The solution obtained was diluted with deionized water to exactly 5.0 ml aqueous solution. Performance of determining concentration of phosphorus in solution was carried out on ICP-AES.

4.4. General procedure for hydroformylation of higher olefins

Hydroformylation experiments were performed in a 75 ml stainless steel autoclave equipped with magnetic stirrer. Hydroformylation catalysts were formed in situ from catalyst precursor, such as $\text{Rh}(\text{acac})(\text{CO})_2$ or $\text{Ru}_3(\text{CO})_{12}$ with ligands. The autoclave was charged with 1-decene, catalyst precursor, ligand, solvent, and internal standard. The system was flushed five times with 10 atm of CO and checked for leaks. Then the

autoclave was pressurized with CO/H_2 (1/1), and brought to the required temperature in a thermostatic oil bath. After appropriate time, the samples were taken from the reaction products to be analyzed by GC-MS.

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