

# Rh/TMPGP complex catalyzed hydroformylation of *p*-isobutylstyrene in thermoregulated PEG biphasic system

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## Abstract

A series of novel phosphite ligands tri-(methoxyl polyethylene glycol)-phosphite (TMPGP) (**1a–1d**) have been synthesized and used in the rhodium-catalyzed hydroformylation of *p*-isobutylstyrene (IBS) in thermoregulated polyethylene glycol (PEG) biphasic system. Under the conditions of  $P = 5.0$  MPa ( $H_2:CO = 1:1$ ),  $P/Rh = 13$  (molar ratio), reaction time = 2 h and temperature = 120 °C, the conversion of IBS was 100% and the yield of aldehyde was 96%. The catalyst could be easily separated from the product by phase separation and reused for nine times without evident loss of activity.

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**Keywords:** Phosphite ligand; Thermoregulated PEG biphasic system; IBS; Hydroformylation; Rhodium

## 1. Introduction

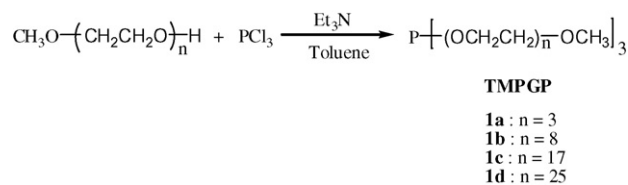
To overcome the difficulty of separating the catalyst from the product in homogeneous catalysis, liquid/liquid biphasic catalysis has been advanced [1]. The most commonly used process is the catalysis in aqueous/organic biphasic systems, consisting of an aqueous phase containing water-soluble catalyst and another phase of either a hydrocarbon or any other solvent of low polarity [2]. However, this process was unsuitable for higher olefins due to their low water-solubility. In order to solve this problem, many improved aqueous/organic biphasic systems have been proposed [3,4]. Based on the property of cloud point (Cp) of nonionic phosphine ligands with PEG chains, Jin and co-workers proposed a novel idea of thermoregulated phase-transfer catalysis (TRPTC) [5,6]. But aqueous/organic biphasic processes are not suitable for water-sensitive systems. This has stimulated the development of nonaqueous liquid/liquid biphasic systems. Horvath and Rabai described a fluorinated biphasic system (FBS), which consists of a fluorinated phase containing a phosphine ligand with fluorinated ponytails and another organic phase. This thermoregulated nonaqueous liquid/liquid biphasic system has been applied in the hydroformylation of higher olefins [7].

Being a non-toxic and inexpensive solvent of low volatility, PEG has drawn much attention of chemists recently as a recyclable solvent medium. One approach is that PEG was used as a reaction medium and after reaction is complete, products were extracted by other immiscible organic solvent. Chandrasekhar et al. studied Heck reaction in PEG and extracted the product with ether at the end of the reaction [8]. As an alternative method, a temperature-dependent biphasic system, composed of PEG 1000, toluene and methyl linoleate (CML), was studied and used in the rhodium catalyzed cooligomerization of CML with ethylene [9]. In addition, Loh and co-workers have described an organic biphasic system containing PEG 3350, heptane and either  $CH_2Cl_2$  or  $CH_3OH$ . This system has been tested in the hydrogenation of 1-hexene [10].

In our previous work, a thermoregulated PEG biphasic system composed of PEG 4000, toluene and heptane was developed, which is characterized by the homogeneous reaction coupled with biphasic separation. The catalyst can be simply recycled. However, the loss of Rh in the upper product-containing phase is still 3% or so after using for four times [11].

In this paper, with the aim to enlarge the application scope of thermoregulated PEG biphasic system and further decrease the loss of Rh, a series of novel phosphite ligands TMPGP (**1a–1d**) have been synthesized (Scheme 1) and used in the rhodium-catalyzed hydroformylation of *p*-isobutylstyrene (IBS) in thermoregulated PEG biphasic system.

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Scheme 1. Synthesis of phosphite ligands TMPGP (**1a–1d**).

## 2. Experimental

### 2.1. Materials and methods

Organic solvents were purified by distillation from an appropriate drying agent under inert atmosphere. IBS was prepared as previously described [12].  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  was used as received from Beijing Research Institute of Chemical Industry without any further purification.

Gas chromatographic analyses were performed by using a gas chromatograph “GC-8810” equipped with a flame ionization detector, a capillary column (OV-101, 30 m  $\times$  0.3 mm, carrier gas: 0.2 MPa  $\text{N}_2$ ) and a Shimadzu C-R3A integrator. *n*-Decane was used as the internal standard. ICP-OES analyses were carried out on an Iris Interpid DUO ER/S (Thermo Elemental, USA).  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Varian INOVA instrument at 400, 100 and 162 MHz, respectively. Chemical shifts (ppm) are given relative to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$  NMR).

### 2.2. Synthesis of phosphite ligands TMPGP (**1a–1d**) and Rh/TMPGP complex catalyst

In a typical experiment (**1a**), all operations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. After the clean and dry 250 ml three neck round-bottomed flask was flushed completely with nitrogen, 35.8 mmol polyethylene glycol monomethyl ether, 38.4 mmol triethylamine and 100 ml toluene were added to the flask. Then, the mixture was cooled to 0 °C with stirring and the mixture of 11.7 mmol  $\text{PCl}_3$  and 20 ml toluene was added dropwise for 1 h. After the completion of the addition, the mixture was stirred for additional 9 h. After filtration, toluene was removed from filtrate under reduced pressure to afford a colorless liquid product. Analytical

data of **1a** were as follows:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  3.904–3.860 (m), 3.412–3.379 (m), 3.280–3.256 (m), 3.053 (s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  = 72.420, 71.479, 71.433, 71.059, 70.016, 70.947, 70.902, 61.968, 61.869, 58.749;  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{H}_5\text{CH}_3$ , 25 °C):  $\delta$  = 139.94. Synthesis of TMPGP (**1b–1d**) is similar with that of **1a**. The Rh/TMPGP complex catalyst was prepared in situ.

### 2.3. Hydroformylation of IBS

All hydroformylation reactions were carried out in a 75 ml standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all experiments performed. The autoclave was charged with PEG 4000, heptane, toluene, IBS,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , TMPGP and *n*-decane and flushed three times with 2.0 MPa CO. The reactor was pressurized with syngas ( $\text{H}_2:\text{CO} = 1:1$ ) up to the required pressure and held at the scheduled temperature with magnetic stirring for a fixed length of time. Then the reactor was cooled to room temperature and depressurized. The upper organic phase was separated by phase separation from the lower PEG phase and immediately analyzed by GC.

## 3. Results and discussion

### 3.1. Loss of ligands in the upper organic phase

Data in Table 1 indicate the loss of ligand in the upper organic phase. With increasing of miscibility temperature, the loss of two phosphite ligands in the upper organic phase all decreases. However, compared with our previously reported octylpolyglycol-phenylene-phosphite (OPGPP), the loss of TMPGP (**1a**) in the upper organic phase is less. Based on data in Table 1, we suggest that the loss of rhodium in the upper organic phase will decrease while using Rh/TMPGP complex as catalyst.

### 3.2. Hydroformylation of IBS in thermoregulated PEG 4000/toluene/heptane system catalyzed by Rh/TMPGP complex

#### 3.2.1. Effect of reaction temperature

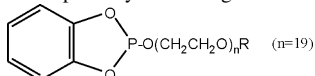
The effect of temperature on the hydroformylation of IBS is shown in Table 2. Under experimental conditions, the conversion

Table 1  
Loss of ligands in the upper organic phase at different miscible temperatures

Entry	Ligand	Miscible temperature <sup>a</sup> (°C)	Loss of ligand in the upper organic phase (mol%)
1	TMPGP ( <b>1a</b> )	60	1.2
2	TMPGP ( <b>1a</b> )	90	0.9
3	TMPGP ( <b>1a</b> )	110	0.4
4	OPGPP <sup>b</sup>	60	3.8
5	OPGPP	90	2.9
6	OPGPP	110	2.2

<sup>a</sup> The temperature that thermoregulated PEG biphasic system changes from biphasic to monophasic.

<sup>b</sup> The structure of OPGPP is as follows:



OPGPP

Table 2  
Effect of reaction temperature on the hydroformylation of IBS catalyzed by Rh/**1a** complex<sup>a</sup>

Entry	Temperature (°C)	Conversion (%)	Aldehyde yield (%)	<i>b/n</i> ratio <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1	100	28	28	1.3	140
2	110	89	89	1.3	445
3	115	97	97	1.1	485
4	120	100	96	1.2	480
5	130	100	98	1.1	490
6	100 <sup>d</sup>	80	79	1.2	395
7	115 <sup>e</sup>	78	77	1.3	385

<sup>a</sup> Reaction conditions: PEG 2.0 g, PEG 4000/toluene/heptane = 2/3/1 (wt. ratio), *P* = 5.0 MPa (H<sub>2</sub>:CO = 1:1), IBS/Rh = 1000 (molar ratio), *P*/Rh = 13 (molar ratio), RhCl<sub>3</sub>·3H<sub>2</sub>O 1.4 mg, *n*-decane 0.1 ml, and reaction time 2 h.

<sup>b</sup> *b* denotes branched aldehyde, *n* denotes normal aldehyde.

<sup>c</sup> Turnover frequency (TOF) in mole of yield per mole of catalyst per hour.

<sup>d</sup> Only toluene was used as the upper layer organic solvent.

<sup>e</sup> Only heptane was used as the upper layer organic solvent.

of IBS and yield of aldehyde all increase with the increase of temperature. When the temperature is increased from 100 °C to 110 °C, the conversion of IBS increases sharply. This may be due to the fact that the system changes from biphasic to monophasic. In order to prove the inference, hydroformylation of IBS was studied by using only toluene as the upper layer organic solvent (the system was homogeneous) at 100 °C (entry 6, Table 2) and heptane as upper layer organic solvent (the system was biphasic) at 115 °C (entry 7, Table 2). These results indicate that PEG biphasic system changes from biphasic to monophasic between 100 °C and 110 °C.

### 3.2.2. Effect of total pressure

Table 3 gives the effect of total pressure (H<sub>2</sub>:CO = 1:1) on the hydroformylation of IBS. With the increase of total pressure, the conversion of IBS and yield of aldehyde all increase. However, when the total pressure is over 5.0 MPa, only a slight increase in yield is observed. Therefore, the optimum total pressure is 5.0 MPa.

### 3.2.3. Effect of reaction time

Data in Table 4 illustrate the effect of reaction time on the hydroformylation of IBS. The conversion of IBS and yield of

Table 3  
Effect of total pressure on the hydroformylation of IBS catalyzed by Rh/**1a** complex<sup>a</sup>

Entry	Pressure (MPa)	Conversion (%)	Aldehyde yield (%)	<i>b/n</i> ratio	TOF (h <sup>-1</sup> )
1	2	64	61	1.0	305
2	3	90	86	1.0	430
3	4	98	94	1.1	470
4	5	100	96	1.2	480
5	6	100	97	1.2	485

<sup>a</sup> Reaction conditions: *T* = 120 °C, other conditions are the same as those in Table 2 except that the total pressure is varied.

Table 4  
Effect of reaction time on the hydroformylation of IBS catalyzed by Rh/**1a** complex<sup>a</sup>

Entry	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	<i>b/n</i> ratio	TOF (h <sup>-1</sup> )
1	0.5	30	29	1.1	580
2	1	86	82	1.1	820
3	2	100	96	1.2	480
4	3	100	97	1.2	323

<sup>a</sup> Reaction conditions: *T* = 120 °C, other conditions are the same as those in Table 2 except that the reaction time is varied.

Table 5  
Effect of *P*/Rh molar ratio on the hydroformylation of IBS catalyzed by Rh/**1a** complex<sup>a</sup>

Entry	<i>P</i> /Rh (molar ratio)	Conversion (%)	Aldehyde yield (%)	<i>b/n</i> ratio	TOF (h <sup>-1</sup> )
1	3	93	88	1.1	440
2	6	94	90	1.1	450
3	13	100	96	1.2	480
4	21	98	93	1.3	465
5	30	96	91	1.3	455

<sup>a</sup> Reaction conditions: *T* = 120 °C, other conditions are the same as those in Table 2 except that *P*/Rh molar ratio is varied.

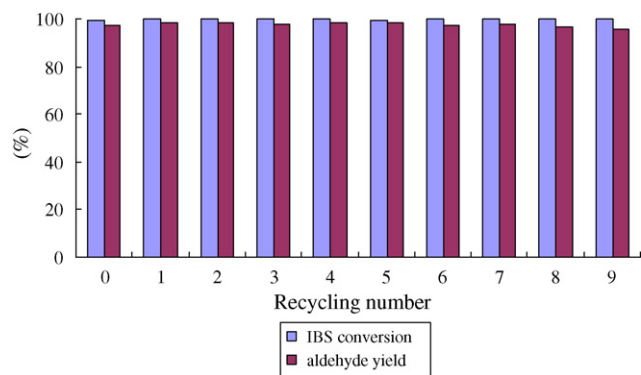


Fig. 1. The recovery efficiency of the Rh/1a complex on the hydroformylation of IBS.

aldehyde increases with the increase of reaction time. When the reaction time was over 2 h, only a slight increase of yield is observed. Therefore, the optimum reaction time is 2 h.

### 3.2.4. Effect of *P/Rh* molar ratio

Generally, reactions using metal complex as catalyst requires excessive ligands in order to increase the stability of catalyst. However, large amounts of ligands will decrease the reaction activity. The effect of *P/Rh* molar ratio on the hydroformylation of IBS is shown in Table 5. It can be seen that the conversion of IBS and yield of aldehyde increase slightly when the *P/Rh* molar ratio is changed from 3 to 13. However, further increasing of *P/Rh* molar ratio will decrease the conversion of IBS and yield of aldehyde. Thus, the optimum *P/Rh* molar ratio is chosen to be 13.

### 3.2.5. Recovery efficiency of the Rh/TMPGP complex catalyst

When the reaction was complete, the upper organic phase was separated from the lower catalyst-containing PEG phase by decantation. Then by adding fresh solvent and substrate, the catalyst can be directly recycled. Fig. 1 illustrates the

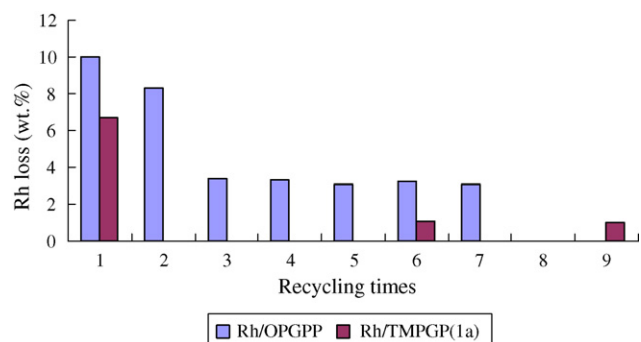


Fig. 2. Loss of rhodium in the upper organic phase.

results of catalyst recovery efficiency on the hydroformylation of IBS. Under the conditions of  $T = 120\text{ }^{\circ}\text{C}$ ,  $P = 5.0\text{ MPa}$ ,  $\text{IBS/Rh} = 1000$ ,  $P/\text{Rh} = 13$ , the Rh/1a complex catalyst could be reused for nine times without evident loss of activity. Moreover, recovered Rh/1b, Rh/1c and Rh/1d complex catalysts could also be used for nine times and no evident loss in activity has been observed. Though the catalyst can be simply recycled, small amounts of Rh were still detected in the upper organic phase. From results of the ICP-OES analysis shown in Fig. 2, it can be seen that the loss of Rh decreases with the increase of recycling times. From the sixth recycling time on, the loss of rhodium in the upper organic phase is around 1% (wt%) lower than that of Rh/OPGPP complex catalyst.

## 4. Conclusions

A series of novel phosphite ligands TMPGP containing polyethylene glycol moiety have been prepared and used as ligands in the rhodium-catalyzed hydroformylation of IBS in thermoregulated PEG biphasic system. Compared with our previously reported phosphite ligand OPGPP, the synthesis of phosphite ligands TMPGP is easier and the loss of rhodium in the upper organic phase decreases.

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