

# Thermoregulated phase transfer ligands and catalysis XVIII: synthesis of *N,N*-dipolyoxyethylene-substituted-2- (diphenylphosphino)phenylamine (PEO–DPPPA) and the catalytic activity of its rhodium complex in the aqueous–organic biphasic hydroformylation of 1-decene

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## Abstract

A novel water soluble phosphine, *N,N*-dipolyoxyethylene-substituted-2-(diphenylphosphino)phenylamine (PEO–DPPPA), was synthesized by a two-step ethoxylation of 2-(diphenylphosphino)phenylamine (2-Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, DPPPA). In the first step, DPPPA was ethoxylated without catalyst to give an intermediate with an average polyethylene glycol (PEG) chain length ( $L = m + n$ ) of 3. Thereafter, this intermediate was further ethoxylated by using KOH as a catalyst to obtain the products with needed values of  $L$ . The solubility of the products in water increases with increasing of  $L$ . When  $L$  is more than 35, the products are water-soluble and possess the property of inverse temperature-dependent solubility in water (cloud point,  $C_p$ ) as nonionic surfactants. The PEO–DPPPA/Rh complex catalyst formed in situ by RhCl<sub>3</sub>·3H<sub>2</sub>O and PEO–DPPPA ( $L = 45$ ) has been applied to the aqueous–organic biphasic hydroformylation of 1-decene. The conversion of olefin and the yield of aldehyde are 99.5 and 99.0%, respectively, under the conditions of 120 °C, 5.0 MPa (CO/H<sub>2</sub> = 1), P/Rh = 4 (molar ratio), 1-decene/Rh = 1000 (molar ratio) and 5 h. Recycling test shows that both the conversion of olefin and the yield of aldehyde are still higher than 94.0% even after the catalyst has been recycled 20 times. The high reactivity of PEO–DPPPA/Rh complex can be attributed to a process termed thermoregulated phase transfer catalysis.

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**Keywords:** Thermoregulated phase transfer catalysis; Hydroformylation; Thermoregulated phosphine; High olefins

## 1. Introduction

It was a milestone in the chemistry of aqueous–organic biphasic catalysis that Ruhrchemie AG for the first time industrially realized the aqueous–organic biphasic hydroformylation of propene catalyzed by triphenylphosphine trisulfonate (TPPTS)/Rh complex in 1984 [1]. However, for higher olefins ( $\geq C_6$ ) the previously mentioned process often suffers from low

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reaction rates caused by the poor solubility of higher olefins in water. To solve this problem a variety of approaches have been developed [2–5]. Recently, a concept of “thermoregulated phase-transfer catalysis” (TRPTC) based on the nonionic water-soluble phosphine-modified rhodium complexes has been successfully applied to the aqueous–organic biphasic hydroformylation of higher olefins [6–8]. In view of the principle of TRPTC, a series of nonionic surface-active water-soluble phosphines by introducing polyoxyethylene moieties to organophosphines possessing the same property of inverse temperature-dependent solubility in water (cloud point,  $C_p$ ) as nonionic surfactants have been synthesized [9–11]. However, the syntheses of nonionic surface-active phosphines are focused on introducing the polyoxyethylene moieties into the hydroxyl groups and sulfonamide of organophosphines. At present, we are interested in developing a new family of nonionic phosphines by introducing the polyoxyethylene moieties into the amino group of organophosphines. In this paper, we report on a synthesis of a novel nonionic water-soluble phosphine (PEO–DPPPA) by a two-step ethoxylation of 2-(diphenylphosphino)phenylamine (2-Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, DPPPA) and the catalytic behavior of its rhodium complex in the aqueous–organic biphasic hydroformylation of 1-decene.

## 2. Experimental

### 2.1. General methods

All organic solvents were purified by distillation from appropriate drying agents under inert atmosphere. RhCl<sub>3</sub>·3H<sub>2</sub>O was purchased from the Beijing Research Institute of Chemical Industry. 1-Decene was purchased from Aldrich Chemical Co. The catalyst was prepared in situ with RhCl<sub>3</sub>·3H<sub>2</sub>O as a catalyst precursor and PEO–DPPPA ( $L = 45$ ) as a ligand. Gas chromatographic analyses were run on a SP-09 instrument (OV-101, 50 m × 0.3 mm capillary column, carrier gas: 0.2 MPa N<sub>2</sub>, FID detector) equipped with a Shimadzu C-R3A integrator using cyclohexane as internal standard. <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded on a JEOL FX-90Q spectrometer using Me<sub>4</sub>Si as standard in CDCl<sub>3</sub>. IR spectra were recorded on a Nicolet 20DX-B spectrometer. Mass

spectra were measured on a Finnigan 312/SS 200 GC–MS.

### 2.2. Preparation of 2-Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (DPPPA)

2-Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (DPPPA) was synthesized according to Cooper et al. [12]. Yield: 75%; <sup>1</sup>H NMR ( $\delta$ , ppm): 3.7–4.0 (b, 2H, NH<sub>2</sub>), 6.5–7.5 (m, 14H, Ar–H); <sup>31</sup>P NMR ( $\delta$ , ppm): –20.5; FT–IR (KBr:  $\nu$ , cm<sup>–1</sup>): 3438, 3362, 1612, 745.

### 2.3. Preparation of *N,N*-dipolyoxyethylene-substituted-2-(diphenylphosphino)phenylamine (PEO–DPPPA)

The ethoxylation of DPPPA was carried out in an 80 ml glass autoclave equipped with an ethylene oxide dispenser and a magnetic stirrer. One gram (3.6 mmol) of DPPPA and 3 ml of anhydrous ethanol were added into the autoclave. The system was purged with nitrogen and heated to 100 °C. Then the desired amount of ethylene oxide (EO) was added to maintain a pressure of 0.4 MPa for 8 h. After ethoxylation, the solvent was removed in vacuum and PEO–DPPPA ( $L = 3$ ) left in the autoclave. Then 20 mg KOH and 3 ml of toluene were added. The autoclave was purged with nitrogen and heated to 100 °C. Ethylene oxide was then added to maintain a pressure of 0.4 MPa. After desired amount of ethylene oxide was added, the reaction was continued for 30 min. Toluene was then drawn out in vacuum giving a yellowish waxy solid product. The average length of PEG chain ( $L$ ) was determined by <sup>1</sup>H NMR spectroscopy. For the PEO–DPPPA ( $L = 45$ ), analytical data were: <sup>1</sup>H NMR ( $\delta$ , ppm): 6.8–7.9 (m, 14H, Ar–H), 3.5–3.8 (br, s, 178H, –CH<sub>2</sub>O, –OH); <sup>13</sup>C NMR ( $\delta$ , ppm): 133.4, 132.5, 131.3, 128.1, 127.6, 78.9, 75.8, 72.1, 70.0, 60.1, 42.3; <sup>31</sup>P NMR ( $\delta$ , ppm): –21.4; FT–IR (KBr:  $\nu$ , cm<sup>–1</sup>): 3422, 2883, 1588, 1467, 1280, 1116, 843.

### 2.4. General procedure for hydroformylation of 1-decene

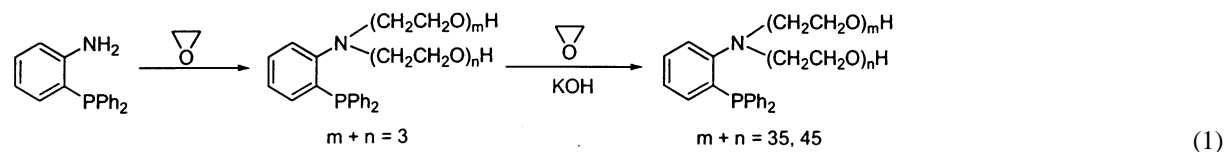
Hydroformylation reaction was carried out in a 75 ml stainless autoclave immersed in an oil bath. The stirring rate was constant for all the experiments. To the autoclave 1.4 mg (5.3  $\mu$ mol) of RhCl<sub>3</sub>·3H<sub>2</sub>O, 21.2  $\mu$ mol of PEO–DPPPA, 740 mg (5.3 mmol) of

1-decene, 0.2 ml of cyclohexane (internal standard), 3.0 ml H<sub>2</sub>O and 2.0 ml toluene were added. The reactor was sealed and flushed five times with 1.0 MPa of CO and then charged with CO/H<sub>2</sub> (CO/H<sub>2</sub> = 1/1) to the given pressure. It was placed in an oil bath preheated to the designated temperature for 5 h and then was cooled down to room temperature and depressurized. The organic phase was separated and dried over anhydrous MgSO<sub>4</sub> and analyzed by gas chromatography immediately. Products were identified by GC–MS by comparing with the standard spectrum.

### 3. Results and discussion

#### 3.1. Synthesis of PEO–DPPPA and its property of inverse temperature-dependent water-solubility

The nonionic water-soluble phosphine PEO–DPPPA was synthesized by a two-step ethoxylation of DPPPA. The synthetic route is shown in Eq. (1).



In the first step, DPPPA was ethoxylated without catalyst to give an intermediate with an average PEG chain length ( $L = m + n$ ) of 3. Thereafter, this intermediate was further ethoxylated by using KOH as a catalyst to obtain the products with different values of  $L$ . The solubility of the products increases with increasing of  $L$ . When  $L$  is more than 35, the products are water-soluble and possess the property of inverse temperature-dependent solubility in water (cloud point,  $C_p$ ). Table 1 gives the cloud point of PEO–DPPPA with different values of  $L$ , which

Table 1  
The cloud point of PEO–DPPPA with different polyoxyethylene chain length<sup>a</sup>

Entry	$L = m + n$	Cloud point (°C)
1	35	80
2	45	92

<sup>a</sup> Cloud point, determined in 2.0% (w/w, aq.) solutions of PEO–DPPPA.

shows the cloud point increase with increasing the polyoxyethylene chain length.

#### 3.2. Hydroformylation of 1-decene catalyzed by Rh/PEO–DPPPA

The aqueous–organic biphasic hydroformylation of 1-decene was carried out using Rh/PEO–DPPPA as the catalyst, which was prepared in situ by RhCl<sub>3</sub>·3H<sub>2</sub>O and PEO–DPPPA ( $L = 45$ ). The effects of temperature, total pressure, the molar ratio of PEO–DPPPA to rhodium and the molar ratio of substrate to rhodium were investigated.

The effect of temperature on the hydroformylation of 1-decene is shown in Table 2. Under the used conditions, both the conversion of 1-decene and the yield of aldehydes increase with increasing of temperature. However, the ratio of normal to branched aldehyde products (n/b) decreases as the temperature increases. The reason for this is that the isomerization of the  $\alpha$ -olefin to internal olefin becomes faster at higher

temperature. The conversion of 1-decene increases from 64.0 to 84.2% while the temperature raises from 90 to 100 °C, which shows that the rhodium catalyst stays in the aqueous phase at a lower temperature

Table 2  
Effect of temperature on the biphasic hydroformylation of 1-decene<sup>a</sup>

Temperature (°C)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h <sup>-1</sup> ) <sup>b</sup>
70	54.5	54.2	2.10	271
80	60.3	60.0	2.06	300
90	64.0	63.7	0.82	318
100	84.2	83.6	0.75	418
110	88.6	88.2	0.65	441
120	94.6	94.0	0.64	470

<sup>a</sup> Reaction conditions:  $P = 5.0$  MPa (CO:H<sub>2</sub> = 1); 1-decene 5.3 mmol; S/Rh = 1000 (molar ratio); PEO–DPPPA  $L = 45$ ; P/Rh = 4 (molar ratio); toluene 2.0 ml; cyclohexane 0.2 ml; degassed H<sub>2</sub>O 3.0 ml; time 2.0 h.

<sup>b</sup> Average turnover frequency: TOF (h<sup>-1</sup>) = h<sup>-1</sup> × mol (aldehyde)/mol (rhodium).

Table 3

Effect of total pressure on the biphasic hydroformylation of 1-decene<sup>a</sup>

Total pressure (MPa)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h <sup>-1</sup> )
2.0	31.4	31.4	0.60	157
3.0	56.3	56.1	0.61	280
4.0	82.2	81.7	0.62	408
5.0	94.6	94.0	0.64	470

<sup>a</sup>  $T = 120\text{ }^{\circ}\text{C}$ ; all other conditions are the same as in Table 2.

( $T < C_p$ ,  $92\text{ }^{\circ}\text{C}$ ) and transfers into the organic phase at a higher temperature ( $T > C_p$ ,  $92\text{ }^{\circ}\text{C}$ ). The optimum temperature for the reaction under the used conditions is  $120\text{ }^{\circ}\text{C}$  resulting in high TOF ( $470\text{ h}^{-1}$ ), conversion (94.6%) and yield of aldehyde (94.0%).

Table 3 gives the influence of total pressure on the hydroformylation of 1-decene. Conversion and aldehyde yield increase with increasing of the total pressure ( $\text{CO}:\text{H}_2 = 1$ ). Meanwhile, the n/b ratio almost remains constant. A pressure of 5.0 MPa was chosen for all hydroformylation reactions.

Table 4 shows the results of hydroformylation of 1-decene with various molar ratio of substrate to rhodium (S/Rh). With increasing of S/Rh, conversion and yield of aldehydes decrease. When the S/Rh ratio is lower than 10,000, conversion of 1-decene and yield of aldehydes all exceed 90%. When the S/Rh ratio is 2000, the reaction can be finished within 5 h. Further increasing of the S/Rh ratio is not necessary. The n/b ratio of aldehydes slightly decreases with the increase of S/Rh ratio.

Table 4

Effect of S/Rh (molar ratio) on the biphasic hydroformylation of 1-decene<sup>a</sup>

S/Rh (molar ratio)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h <sup>-1</sup> )
1000	99.5	99.0	0.62	198
2000	99.4	99.0	0.58	396
3325	96.9	96.4	0.51	641
6650	95.6	95.1	0.45	1265
10000	91.4	90.2	0.45	1804
13300	85.6	85.0	0.44	2261
26600	79.8	79.3	0.42	4218

<sup>a</sup>  $T = 120\text{ }^{\circ}\text{C}$ ; time 5 h; all other conditions are the same as in Table 2.

Table 5

Effect of PEO–DPPPA/Rh (molar ratio) on the biphasic hydroformylation of 1-decene<sup>a</sup>

PEO–DPPPA/Rh (molar ratio)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h <sup>-1</sup> )
0	18.6	18.5	2.50	92
1	85.6	85.2	0.54	426
2	93.2	92.5	0.62	462
4	94.6	94.0	0.64	470
8	95.0	94.5	0.65	472
12	94.7	94.1	0.64	470

<sup>a</sup>  $T = 120\text{ }^{\circ}\text{C}$ ; all other conditions are the same as in Table 2.

The effect of PEO–DPPPA/Rh molar ratio on the hydroformylation of 1-decene is shown in Table 5. It can be seen in Table 5 that the conversion and yield of aldehyde increase sharply while the PEO–DPPPA/Rh ratio varies from 0 to 1. When the PEO–DPPPA/Rh ratio is between 2 and 12, the results change smoothly. At PEO–DPPPA/Rh = 4, the conversion of 1-decene reaches 94.6% and the yield of aldehydes is 94.0%. Further increasing of the P/Rh ratio shows no influence on the catalyst activity.

Table 6

Recycling efficiency of the PEO–DPPPA ( $L = 45$ )/Rh catalyst in the aqueous–organic biphasic hydroformylation of 1-decene<sup>a</sup>

Enter	Conversion (%)	Yield of aldehyde (%)	TOF (h <sup>-1</sup> )
1	99.5	99.0	198
2	99.2	98.7	197
3	99.3	99.0	198
4	99.1	98.7	197
5	98.8	98.2	196
6	98.0	97.6	195
7	95.2	94.7	189
8	98.5	98.0	196
9	98.8	98.2	196
10	95.6	95.1	190
11	98.8	98.2	196
12	97.6	97.3	195
13	97.9	97.5	195
14	95.2	94.6	189
15	95.4	94.7	189
16	94.8	94.3	189
17	96.7	96.0	192
18	96.1	95.4	191
19	95.4	94.8	189
20	95.1	94.4	189

<sup>a</sup>  $T = 120\text{ }^{\circ}\text{C}$ ; Time 5 h; all other conditions are the same as in Table 2.

### 3.3. Recycling efficiency of the PEO–DPPPA/Rh catalyst

Recycling experiments were designed to test the recycling efficiency of the catalyst. When the reaction is complete, the organic phase is separated from the reaction system by decantation and the catalyst stays in the aqueous phase. Then, by adding fresh organic solvent and substrate the catalyst can be directly recycled. Table 6 gives the results of catalyst recycling in the hydroformylation of 1-decene. After recycling for 20 times, both the conversion of 1-decene and the yield of aldehyde are still as high as 95.1 and 94.4%, respectively. The reason for this may be that PEO–DPPPA is a P–N bidentate ligand, which leads to a more stable thermoregulated phase transfer rhodium complex catalyst. We are studying further to reveal the nature of the coordination between rhodium and PEO–DPPPA.

## 4. Conclusions

A novel nonionic water-soluble phosphine ligand PEO–DPPPA has been synthesized by a two-step ethoxylation of DPPPA. This phosphine demonstrates the character of inverse temperature-dependent water solubility ( $C_p$ ). The PEO–DPPPA/Rh catalyst formed in situ by  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and PEO–DPPPA ( $L = 45$ ) shows a high activity and excellent recycling efficiency in the aqueous–organic biphasic hydroformylation of

1-decene through a process termed thermoregulated phase transfer catalysis (TRPTC).

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