Thermoregulated phase transfer ligands and catalysis XIV Synthesis of *N,N*-dipolyoxyethylene-substituted-4-(diphenylphosphino) benzenesulfonamide (PEO-DPPSA) and the catalytic activity of its rhodium complex in hydroformylation of 1-decene

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Abstract

A novel water soluble phosphine, *N,N*-dipolyoxyethylene-substituted-4-(diphenylphosphino) benzenesulfonamide (PEO-DPPSA), is synthesized by ethoxylation of 4-(diphenylphosphino) benzenesulfonamide $Ph_2P–C_6H_4SO_2NH_2$ (DPPSA) obtained from palladium-catalyzed P–C coupling reaction between $4-I–C_6H_4SO_2NH_2$ and Ph_2PH. The PEO-DPPSA possesses the same property of inverse temperature-dependent solubility in water (cloud point, C_p) as nonionic surfactants. Investigation on the behavior of $RhCl_3 \cdot 3H_2O$/PEO-DPPSA complex in the aqueous–organic biphasic hydroformylation of 1-decene showed that the complex exhibited high catalytic activity. The conversion of 1-decene and the yield of aldehydes reach as high as 97.8 and 95.6%, respectively, under optimized conditions. The high reactivity of Rh/PEO-DPPSA complex can be attributed to a process termed thermoregulated phase transfer catalysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nonionic water-soluble phosphine; Thermoregulated phase transfer catalysis; Hydroformylation; 1-Decene; Cloud point

1. Introduction

Synthesis of water-soluble phosphines is one of the most active areas nowadays in organometallic chemistry research. In 1984, the aqueous–organic biphasic hydroformylation of propene catalyzed by triphenylphosphine trisulfonate (TPPTS)/Rh complex was first realized industrially at Ruhrchemie AG in Oberhausen/Germany [1,2]. Usually ligands comprising catalyst complexes used in biphasic catalysis are phosphines with ionic substituents (sulfonic and carboxylic acids, quaternary alkyl/aryl ammonium groups) [3]. However, catalysts with nonionic ligands, such as phosphino alcohols [4], phosphines with polyether substituents [5,6], crown ether substituted phosphines [7] and carbohydrate-substituted phosphines [8] have been the subject of attention in connection of biphasic catalysis for many years.
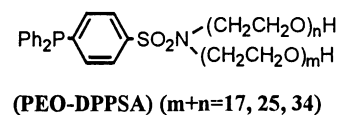
Recently, a series of nonionic water-soluble phosphine ligands bearing polyoxyethylene moieties have been synthesized [9–11]. With polyoxyethylene chains as the hydrophilic group in the molecular structure, the ligands demonstrate a special property of inverse temperature-dependent solubility in water

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similar to that of nonionic surfactants. As a result, their metal complexes are soluble in the aqueous phase at low temperature and can precipitate from water and transfer into the organic phase on heating to a temperature above the critical temperature–cloud point (C_p). Such a process, called "thermoregulated phase transfer catalysis (TRPTC)", has been applied successfully in the hydroformylation of higher olefins in aqueous–organic biphasic media [12,13]. It not only provides a meaningful solution to the problem of catalyst/product separation, but also extricates itself from the limitation of low reaction rates of water-immiscible substrates. The scope of application of biphasic catalysis can be greatly broadened. The present initial study describes the preparation of a novel nonionic water-soluble phosphine (PEO-DPPSA) and the catalytic behavior of it is rhodium complex in the biphasic hydroformylation of higher olefins.

$$Ph_2P-\langle C_6H_4 \rangle-SO_2N\begin{cases}(CH_2CH_2O)_nH \\ (CH_2CH_2O)_mH\end{cases}$$

(PEO-DPPSA) (m+n=17, 25, 34)

Experimental results indicate that PEO-DPPSA do possess a property of inverse temperature-dependent water solubility and the Rh/PEO-DPPSA complex exhibits high activity for the hydroformylation of 1-decene in water-organic biphasic media.

2. Experimental

2.1. General methods

Air- and moisture-sensitive reactions were carried out under N_2 atmosphere. 4-I–$C_6H_4SO_2NH_2$ and Ph_2PH were prepared according to literature procedures [14,15]. 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_2, FID detector) equipped with a Shimadzu C-R3A integrator using cyclohexane as internal standard. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer using Me_4Si and H_3O_4 as standards and their corresponding chemical shifts values were reported in ppm. IR spectra were recorded on Nicolet 20DX-B spectrometer and reported in cm^{-1}. Mass

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

2.2. Preparation of 4-Ph$_2$P–C$_6$H$_4$SO$_2$NH$_2$ (DPPSA)

In a clean, dry 250 ml three neck round-bottomed flask were placed 28.3 g (0.1 mol) of 4-I–$C_6H_4SO_2NH_2$, 11.9 g (0.12 mol) of anhydrous KOAc, 22.4 mg of $Pd(OAc)_2$ and 100 ml of $CH_3CON(CH_3)_2$. The system was flushed three times with nitrogen and heated in an oil bath to 130°C. When the temperature reached 130°C, 18.6 g (0.1 mol) of Ph_2PH was added to the system. The reaction mixture was kept at that temperature for 15 h and then cooled. The contents was poured into 200 ml of distilled water and extracted three times with a total of 350 ml CH_2Cl_2. The extracts were combined, dried and distilled. The resulting brown solid on recrystallizing from 95% ethanol yielded 24.5 g (yield 72%) colorless crystalline product (mp 116–117°C). Analytical data of the product were as follows: ^{1}H NMR (δ, ppm): 4.1–4.2 (b, 2H, –NH_2), 7.4–8.2 (m, 14H, –Ph); ^{31}P NMR (δ, ppm): −6.81; FT–IR (KBr: υ, cm^{-1}): 3346, 3258, 1580, 1161, 750.

2.3. Preparation of N,N-dipolyoxyethylene-substituted 4-(diphenylphosphino) benzenesulfonamide (PEO-DPPSA)

The ethoxylation of DPPSA was carried out in a 80 ml glass autoclave equipped with an ethylene oxide dispenser and a magnetic stirrer. l.9 g (5.5 mmol) of DPPSA together with 20 mg of KOH and 5.0 ml of toluene were added into the autoclave. After being completely flushed with nitrogen, the autoclave was heated to 100°C. Ethylene oxide was then added to maintain a pressure of 0.4 MPa. Gradual reduction of pressure indicated that ethoxylation proceeded smoothly. After the desired amount of ethylene oxide was added, the reaction was continued for 30 min. Toluene was then drawn out under vacuum giving a yellowish waxy solid product. For the PEO-DPPSA ($m + n = 17$), analytical data were: ^{1}H NMR (δ, ppm): 7.3–7.6 (m, 14H, –Ph); 3.4–3.7 (br, s, 70H, –CH_2O, –OH); ^{13}C NMR (δ, ppm): 134, 132, 131, 128, 77, 75, 72, 70, 61, 48; ^{31}P NMR (δ, ppm): −5.22; FT–IR (KBr: υ, cm^{-1}): 3438, 2885, 1467, 1146, 842.

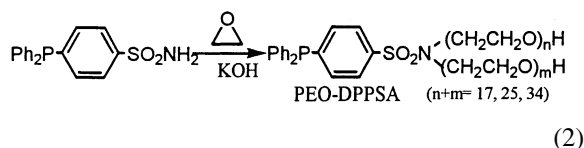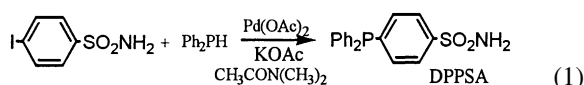### 2.4. General procedure for hydroformylation of 1-decene

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. Into the autoclave were placed 1.4 mg (5.3 μmol) of $RhCl_3 \cdot 3H_2O$, 42.4 μmol of PEO-DPPSA, 0.74 g (5.3 mmol) of 1-decene, 0.2 ml of cyclohexane (internal standard), 3.0 ml of water and 2.0 ml toluene. The reactor was sealed and flushed five times with 1.0 MPa of CO and then charged with CO:H_2 (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 to room temperature and depressurized. The organic phase was dried over anhydrous $MgSO_4$ and analyzed by gas chromatography immediately. Products were identified by GC–MS by comparing with the standard spectra.

3. Results and discussion

3.1. Synthesis of PEO-DPPSA and its property of inverse temperature-dependent water-solubility

Two new compounds the nonionic water-soluble phosphine PEO-DPPSA and its precursor DPPSA were synthesized. Generally, an aryl sulfonamide is prepared by ammonolysis of the corresponding aryl salfonyl chloride. But for the preparation of DPPSA,

such a method is unsuitable, because phosphous atom will be oxidized when diphenylphosphinobenzene-sulfonic acid is treated with $SOCl_2$. Recently, Herd et al. have reported that phosphines can be obtained through the P–C cross coupling reaction [16]. Based on this synthetic strategy, DPPSA was prepared for the first time through the palladium-catalyzed P–C coupling reaction between 4-I-$C_6H_4SO_2NH_2$ and Ph_2PH. Then by subsequent KOH-catalyzed ethoxylation of DPPSA with ethylene oxide, a novel nonionic water-soluble phosphine PEO-DPPSA was obtained. The synthetic route is shown in Eqs. (1) and (2).

$$I\text{-}\langle\rangle\text{-}SO_2NH_2 + Ph_2PH \xrightarrow[\substack{KOAc \\ CH_3CON(CH_3)_2}]{Pd(OAc)_2} Ph_2P\text{-}\langle\rangle\text{-}SO_2NH_2 \quad \text{DPPSA} \qquad (1)$$

$$Ph_2P\text{-}\langle\rangle\text{-}SO_2NH_2 \xrightarrow[KOH]{\overset{O}{\triangle}} Ph_2P\text{-}\langle\rangle\text{-}SO_2N\overset{(CH_2CH_2O)_nH}{\underset{(CH_2CH_2O)_mH}{}} \quad \text{PEO-DPPSA} \quad (n+m=17,25,34)$$

$$(2)$$

In the ethoxylation of DPPSA, the effect of catalyst amount of KOH was investigated (see Fig. 1). The data indicate that ethoxylation rate increases with increasing of the amount of KOH.

It is well known that water solubility of nonionic surfactants with polyoxyethylene moieties as the hydrophilic groups is due to the hydrogen bonds formed between the polyoxyethylene chain and water [17]. But on heated to a certain temperature, the water
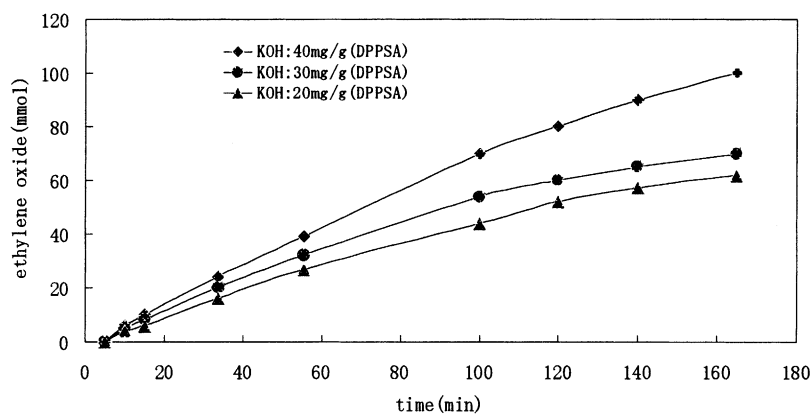

Fig. 1. Effect of catalyst amount of KOH on the ethoxylation rate conditions: DPPSA, 1.9 g (5.5 mmol); toluene, 5.0 ml; T, 100°C; P_{EO}, 0.4 MPa.

Table 1
The cloud point of PEO-DPPSA with different polyoxyethylene chain length[a]

Entry	Value of $(m + n)$ in PEO-DPPSA	Cloud point (°C)
1	17	51
2	25	59
3	34	68

[a] Cloud point, determined in 2.0% (w/w, aq.) solutions of PEO-DPPSA.

solubility of this kind of compounds will decrease sharply and the whole aqueous phase exhibits clouding phenomenon due to the cleavage of hydrogen bonds. This temperature is called cloud point (C_p). Moreover, such a process is reversible, since the water solubility can be restored on cooling to a temperature lower than the cloud point. As we have expected the phosphine PEO-DPPSA, like the nonionic surfactants, also possesses the property of inverse temperature-dependent water solubility-C_p, which is shown in Table 1. The data indicate that the cloud point increases with the increase of the polyoxyethylene chain length.

3.2. Hydroformylation of 1-decene catalyzed by Rh/PEO-DPPSA

The aqueous-organic biphasic hydroformylation of 1-decene was carried out using Rh/PEO-DPPSA as the catalyst, which was prepared in situ from $RhCl_3 \cdot 3H_2O$ and PEO-DPPSA ($m + n = 25$). The effects of temperature, total pressure, the molar ratio of substrate to rhodium and molar ratio of PEO-DPPSA to rhodium molar ratio were investigated.

The effect of temperature on the hydroformylation of 1-decene is shown in Table 2. Under the experimental conditions, 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 temperature increases. The reason is due to the isomerization of the α-olefin to internal olefin becomes faster at higher temperature which has been observed in blank test under conditions without syn-gas. The optimum temperature for the reaction is 100°C considering high TOF (191 h^{-1}), conversion and yield of aldehyde.

The influence of total pressure has also been assessed (Table 3). Conversion and products yield

Table 2
Effect of reaction temperature on biphasic hydroformylation of 1-decene[a]

Temperature (°C)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h^{-1})[b]
70	10.4	10.4	160	21
80	27.0	26.4	1.42	53
90	83.9	81.7	0.98	163
100	97.8	95.6	0.64	191

[a] Reaction conditions: $P = 5.0$ MPa ($CO:H_2 = 1:1$); 1-decene 5.3 mmol; P/Rh $= 8$; toluene 2.0 ml; cyclohexane 0.2 ml; PEO-DPPSA ($m + n = 25$); H_2O 3.0 ml; time 5 h.
[b] Average turnover frequency; TOF (h^{-1})= mol (aldehyde)/mol (Rh).

Table 3
Effect of total pressure on the biphasic hydroformylation of 1-decene[a]

Pressure (MPa)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h^{-1})
3.0	31.4	31.4	0.60	63
4.0	69.0	68.1	0.61	136
5.0	97.8	95.6	0.64	191
6.0	98.2	97.4	0.64	195

[a] $T = 100$°C, all other conditions are the same as in Table 2.

increase with increasing of the total pressure ($CO:H_2 = 1$). Meanwhile, the n/b ratio almost remains constant. A pressure of 5.0 MPa was chosen for this hydroformylation reaction.

Table 4 shows the results of hydroformylation of 1-decene with various molar ratio of substrate to rhodium (S/Rh). With increase of S/Rh, conversion and yield of aldehydes decrease. When the S/Rh ratio is lower than 2000, conversion of 1-decene and yield of aldehyde all exceed 93%. The n/b ratio of aldehyde produced slightly decreases with an increase of S/Rh ratio.

Table 4
Effect of S/Rh ratio on the biphasic hydroformylation of 1-decene[a]

S/Rh (molar ratio)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h^{-1})
1000	98.3	97.0	0.66	194
2000	95.2	93.8	0.64	375
4000	88.6	87.1	0.62	697
5000	80.7	78.9	0.62	789
10000	65.3	64.0	0.60	1280

[a] $T = 100$°C; P/Rh $= 12$, all other conditions are the same as in Table 2.

Table 5
Effect of PEO-DPPSA/Rh molar ratio on the biphasic hydroformylation of 1-decene[a]

PEO-DPPSA/ Rh (molar ratio)	Conversion (%)	Yield of aldehyde (%)	n/b	TOF (h^{-1})
2	63.7	63.1	0.55	126
4	91.4	90.2	0.60	180
8	97.8	95.6	0.64	191
12	98.3	97.0	0.66	194
20	95.5	94.1	0.66	188

[a] $T = 100°C$, all other conditions are the same as in Table 2.

The effect of PEO-DPPSA/Rh molar ratio on the hydroformylation of 1-decene and the results were shown in Table 5.

It can be seen from Table 5 that the conversion and yield of aldehyde increase sharply while PEO-DPPSA/Rh ratio varies from 2 to 4. When the PEO-DPPSA/Rh ratio is between 4 and 20, the results change smoothly. At PEO-DPPSA/Rh = 12, the conversion of 1-decene reaches 98.3% and the yield of aldehydes is 97.0%. As a comparison, Rh/TPPTS (TPPTS: sodium salt of triphenylphosphine trisulfonate) complex, a perfect catalyst in the biphasic hydroformylation of propylene in the RCH/RP process, but when applied to the hydroformylation of higher olefins, the reaction conversion is only about 20% [1,2].

The satisfactory catalytic activity of Rh/PEO-DPPSA ($m + n = 25$) complex is ascribed to a recently developed process termed thermoregulated phase transfer catalysis (TRPTC) [11], which was based on the inverse temperature-dependent water solubility of nonionic water-soluble phosphine ligands. The most notable feature is that the catalyst can back and forth between aqueous phase and organic phase and the direction of transfer is regulated by temperature. That is, at a temperature lower than the cloud point (C_p), the catalyst remains in the aqueous phase. On heating to a temperature higher than the C_p, the catalyst will transfer to the organic phase. Thus, at a reaction temperature which is higher than the C_p, the catalyst and substrate all stay in the organic phase and the reaction proceeds homogeneously. After reaction, on cooling to a temperature lower than the cloud point, the catalyst will return to the aqueous phase and separate from products.

4. Conclusion

A novel nonionic water-soluble phosphine ligand PEO-DPPSA has been designed and synthesized by a two-step procedure. This phosphine ligand is demonstrated to possess the character of inverse temperature-dependent water solubility (C_p). Moreover, its rhodium complex Rh/PEO-DPPSA has shown to be very effective for the biphasic hydroformylation of 1-decene through a process termed thermoregulated phase transfer catalysis (TRPTC).

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