

Letter

Thermoregulated phase transfer ligands and catalysis. I. Synthesis of novel polyether-substituted triphenylphosphines and application of their rhodium complexes in two-phase hydroformylation

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Abstract

A series of novel water-soluble polyether-substituted triphenylphosphines (PETPPs) were prepared by means of the ethoxylation of mono-, di- and tri-*p*-hydroxytriphenylphosphines. PETPPs manifest inverse temperature-dependent solubility in water that enables them to act as thermoregulated phase transfer ligands. The concept of the thermoregulated phase transfer catalysis is successfully applied to the biphasic hydroformylation of higher olefins, such as 1-dodecene, in the presence of rhodium–PETPP complexes as the catalysts.

Keywords: Water-soluble phosphine; Two-phase hydroformylation; Higher olefin; Thermoregulated phase transfer catalysis

Increasing efforts have been recently devoted to the variation of the application phase in liquid/liquid biphasic systems in order to achieve high catalytic activity and selectivity as well as facile catalyst/product separation [1]. Horvath et al. [2] have developed an interesting fluoruous biphasic system, which is based on the limited miscibility of partially or fully fluorinated compounds with non-fluorinated chemicals. An alternative to fluoruous biphasic system has been reported by Bianchini et al. [3]. The strategy involved the use of the solubility gap of metal–sulphur complexes in the methanol/hydrocarbon biphasic system.

Similar to Shell's SHOP process [4], the above described biphasic systems could become one-phase systems at appropriate higher reaction temperature. Upon completion of the reaction, the reaction mixture was cooled to room temperature, and separated into two phases. Thus the recovery of the catalysts could be easily realized.

In this communication, we report our initial work on the synthesis of a series of novel polyether-substituted triphenylphosphines (PETPPs). PETPPs manifest inverse temperature-dependent solubility in water that enables them to act as thermoregulated phase transfer ligands. The concept of the thermoregulated phase transfer catalysis (TRPTC), in which the catalyst transfers into the organic phase to cat-

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alyze the reaction at higher temperature and returns to the aqueous phase to be separated from the product at lower temperature is successfully applied to the biphasic hydroformylation of higher olefins in the presence of Rh–PETPP complexes as the catalysts.

Polyether-substituted phosphines are of interest as recoverable, nonionic, water-soluble ligands. The syntheses of chelating diphosphines with polyether moiety [5–7], crown-functionalized triarylphosphines [8] and smart ligands [9] have been reported so far. However, the synthetic methodology is limited to the reactions between phosphorous compounds and polyether derivatives. It appears worthwhile to try other approaches.

The ethoxylation of compounds with active hydrogen is a main route to prepare nonionic surfactants [10]. We extend this methodology to water-soluble phosphines with polyether moiety. Polyether-substituted triphenylphosphines 2a–2c, could be readily prepared by means of the ethoxylation of mono-, di- and tri-*p*-hydroxytriphenylphosphines (Scheme 1).

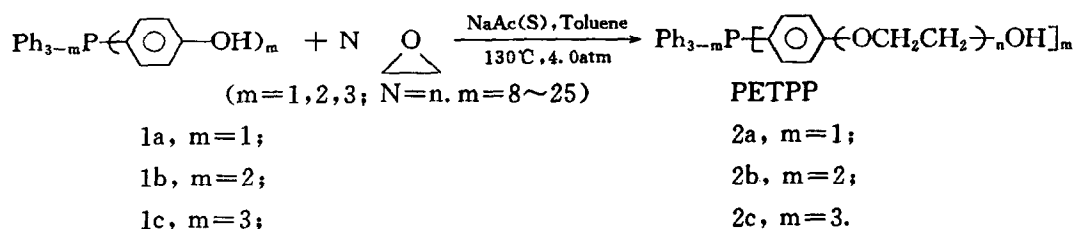
Mono-, di- and tri-*p*-hydroxytriphenylphosphines 1a–1c were prepared by published procedures [11,12]. Ethoxylation was carried out in a 100 ml glass autoclave equipped with an apparatus for continuous ethoxylation. Compounds 1a–1c together with a catalytic amount of anhydrous sodium acetate were dissolved in toluene and charged in the autoclave. The system was purged with nitrogen and heated to 130°C. Then the desired amount of ethylene oxide (EO) was added to maintain a pressure of 4.0 atm (EO/N₂ = 3/1) for the required period of time. After ethoxylation was complete,

toluene was drawn out under vacuum. PETPPs 2a–2c were obtained and could be used without further purification. ¹H NMR spectroscopy was applied to determine the total length of polyether-chain (*N*).

PETPPs are pale yellow viscous liquids (*N* ≤ 20) or waxy solids (*N* > 20) at room temperature depending on the total length of polyether-chain *N*. Solubility determination shows that they are completely soluble in water when *N* ≥ 8. Furthermore, the solubility can be deliberately adjusted by varying the chain length.

It is well known that polyether-substituted nonionic surfactants possess the property of inverse temperature-dependent solubility in water when the hydrophobe to hydrophile ratio is suitable [10]. Namely, they can precipitate from water on heating above a critical temperature-cloud point (*T*_p). One of the explanations of this phenomenon is the cleavage of the hydrogen bonds between the polyether chain and water on heating. As we have expected, PETPPs also have distinct cloud points in the range from 26°C to 95°C (Table 1). On the other hand, the solubility of PETPPs in some nonpolar aprotic solvents, such as toluene and heptane, increases with the rise of temperature. For example, ligand 2a with *N* = 25 appears to form a homogeneous solution in toluene at 100°C, although it is insoluble in the same solvent at room temperature.

The properties described above enable transition metal PETPP complexes to be designed into water-soluble catalysts possessing a thermoregulated phase transfer function in the aqueous/organic two-phase system. That is, the catalyst can transfer into the organic phase to



Scheme 1.

Table 1
Cloud point of PETPPs

Entry	PETPP	<i>M</i>	<i>N</i>	T_p^a (°C)
1	2a	1	8	26
2	2a	1	16	52
3	2a	1	25	75
4	2b	2	15	55
5	2b	2	20	71
6	2c	3	18	~95 (58 ^b)

^a Determined in 3 wt% PETPPs aqueous solution.

^b Determined in 10 wt% NaCl(aq.) solution containing 3 wt% PETPPs.

catalyze the reaction at higher temperature and return to the aqueous phase to be separated from the product at lower temperature. Such a catalytic process, termed the thermoregulated phase transfer catalysis, is fundamentally different from the normal two-phase catalysis, in which the catalyst and the substrate stay in different phases for the biggest part. As shown below, the concept of the thermoregulated phase transfer catalysis is successfully applied to an actual two-phase reaction.

The two-phase hydroformylation of higher olefins was chosen as a model reaction to investigate the tentative idea of TRPTC. Such a reaction is usually unsuccessful because of the low solubility of higher olefins in the aqueous phase where the catalyst exists [13]. The results of the hydroformylation of higher olefins, catalyzed by Rh–PETPP complexes prepared in

situ, are presented in Table 2. The catalysts exhibit very good catalytic properties with the conversion up to 93% and the selectivity for aldehyde about 85%. Several recycles of the catalyst containing aqueous phase after separation are readily carried out without marked loss in catalytic activity and selectivity (entries 6–9 in Table 2). In view of the phase transfer function of PETPPs discussed above, it is reasonable to regard hydroformylation as being carried out in the organic phase rather than in the aqueous phase.

A general description of such a process of the thermoregulated phase transfer catalysis is as follows. At room temperature, almost all Rh–PETPP catalyst remains in the aqueous phase because the partitioning of the catalyst between water and toluene strongly favors the former. On heating to a temperature higher than T_p , however, the catalyst precipitates from water and transfers into toluene, where it transforms olefins into aldehydes. After hydroformylation is complete and the system is cooled to room temperature, the catalyst returns to water. Thus, a simple phase separation enables continuous reuse of the catalyst.

In a system containing two liquid phases, mass transfer control is likely to dominate, which contrasts with the homogeneous system where kinetic control is operative. For those substrates with poor solubility in the aqueous phase, diffi-

Table 2
Hydroformylation of higher olefins catalyzed by Rh–PETPP in the H₂O/toluene system^a

Entry	Cycle ^b	PETPP	<i>N</i>	Olefin	Conversion ^c (%)	Aldehyde selectivity ^c (%)
1	0	2a	16	1-dodecene	95.5	87.5
2	0	2a	25	1-dodecene	96.5	84.7
3	0	2c	18	1-hexene	93.6	90.5
4	0	2c	18	1-octene	97.9	86.1
5	0	2c	18	1-dodecene	96.0	83.2
6	1	2c	18	1-dodecene	96.3	84.0
7	2	2c	18	1-dodecene	96.8	86.1
8	3	2c	18	1-dodecene	94.1	84.7
9	4	2c	18	1-dodecene	94.0	81.5

^a Reaction conditions: $T = 100^\circ\text{C}$. $P = 5.0$ MPa ($\text{CO}/\text{H}_2 = 1/1$), $\text{RhCl}_3 = 1.6 \times 10^{-5}$ mol, $\text{P}/\text{Rh} = 13.0$, olefin 1 ml, H₂O 3 ml, toluene 2 ml, pH = 6.0, for 7 h.

^b Number of catalyst recycles.

^c Determined by gas chromatography (SP-09, OV-101).

culty could be much more outstanding. The strategy of the thermoregulated phase transfer catalysis, in which the catalyst transfers into the organic phase to catalyze the reaction at higher temperature and returns to aqueous phase to be separated from products at lower temperature, provides a potential solution to this problem. At present, further studies are under way to investigate the detailed aspect of the thermoregulated phase transfer catalysis and its applications in the two-phase system.

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