Aqueous biphasic hydroformylation of higher olefins catalyzed by rhodium complexes with amphiphilic ligands of sulfonated triphenylphosphine analog

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The catalytic performances of rhodium complexes with three new amphiphilic phosphine ligands, bis-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (**3**), phenyl-(3-sodium sulfonatophenyl)-(4-*tert*-butyl-phenyl)-phosphine (**4**) and bis-(4-*tert*-butylphenyl)-(3-sodium sulfonatophenyl) phosphine (**5**), in hydroformylation of 1-hexene, 1-octene and 1-dodecene have been studied. The steric attributes of free ligands are investigated by Tolman's cone angle method through geometric optimizations. The results reveal that the new phosphines are surface-active as the typical surfactants and the corresponding rhodium complexes show significant enhancements in the reaction rate and higher selectivities toward the normal aldehydes in comparison with those obtained by triphenylphosphine trisulfonate (TPPTS)- and triphenylphosphine disulfonate (TPPDS) rhodium complexes under identical conditions.

KEY WORDS: amphiphilic phosphine; water-soluble rhodium complex; biphasic hydroformylation; 1-hexene; 1-octene; 1-dodecene.

1. Introduction

Since the commercial establishment of two-phase catalysis for propene hydroformylation in the Ruhrchemie–Rhone-Poulenc process in 1984, the use of metal complex catalysts involving water-soluble ligands has been recognized as an effective method for catalyst product separation [1–4]. The advantages of this technique economically and ecologically compared to the corresponding homogeneous process make the aqueous biphasic catalyst system increasingly important both for industrial application and for new reactions and new products, and become one of the most active research fields currently. Furthermore, it is well established that the main drawback of the aqueous biphasic catalyst system is the low reaction rates due to the phase-transfer limitations caused by poor substrate solubility in the water phase. The lower reaction rate may become economically unviable, particularly in the case of producing commodity chemicals such as aldehydes prepared from olefins [4].

Several attempts have been developed to accommodate the low reaction rate in the aqueous biphasic hydroformylation of higher olefins that have limited water solubility, including, *e.g.*, by addition of cosolvent or surfactant [5–9] and employment of thermoregulated phase-transfer catalysts [10,11], supported aqueous phase catalysts (SAPC) [12,13], amphiphilic ligands [14–26] and so on. Although less well studied than the traditional biphasic approach, recently the amphiphilic concept has attained some interest and a number of amphiphilic phosphines have been synthesized and evaluated in catalysis. Conceptually, two major strategies have been developed for the design of amphiphilic ligands to avoid addition of mass transfer promoters to the reaction medium. One approach is to incorporate the surface-active group(s) into the molecules of ligand [14–21]. Another way is to employ the ligands composed of substituent(s) by which the amphiphilic ligands and complexes can be transferred between an organic and an aqueous phase by simple pH adjustments [22–26].

A simple protocol to obtain a surface-active phosphine ligand may rely on the sulfonation of triarylphosphine bearing linear alkyl groups. But this was unsuccessful because of the cleavage of the alkyl chain during the conventional sulfonation process. Recently, Caron and coworkers have reported that a new family of amphiphilic phosphines can be prepared by reaction of the Grignard reagent $(CH_3)_3CC_6H_4MgBr$ with phosphorus (III) chloride reagents and then sulfonation [27]. The *tert*-butyl group is stable under the sulfonation conditions. The new phosphines show typical surface-active properties and the catalytic performance obtained with one of these phosphines in the palladium-catalyzed cleavage of undecyl allyl carbonate was 24 000 times higher than that obtained with trisulfonated triphenylphosphine (TPPTS) as ligand. However, little is known about the functions of the above amphiphilic phosphines in the aqueous biphasic hydroformylation of

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higher olefins. Herein, we report the catalytic performances of rhodium complexes based on the three amphiphilic phosphines in the hydroformylations of 1-hexene, 1-octene and 1-dodecene. The results have been compared with those obtained with TPPTS and TPPDS as ligands.

2. Experimental

2.1. Ligands and rhodium complexes

2.1.1. General comments

Commercially available reagents, bromo-4-*tert*-butylbenzene (Aldrich), phosphorus (III) chlorides Ph_2PCl and $PhPCl_2$ (Acros) were used without further purification. THF was distilled from sodium/benzophenone under argon before use. All ligand syntheses were carried out with standard Schlenk techniques under argon atmosphere.

2.1.2. Spectroscopy

The structures of phosphines and corresponding rhodium complexes were investigated according to the spectroscopic studies of IR, ^{1}H- and ^{31}P(^{1}H)-NMR. IR spectra were measured on a Nicolet 740 FTIR spectrometer with a resolution of 4 cm^{-1}. NMR spectroscopy was recorded on a Varian FT Unity$^+$ 500 spectrometer. ^{31}P(^{1}H)-NMR spectra were recorded at 200 MHz at room temperature in $CDCl_3$ for organic-soluble compounds and in D_2O for water-soluble ones. The chemical shift was referenced to 85% H_3PO_4. ^{1}H-NMR spectra were referenced to $SiMe_4$. Surface tension was measured by Sigma 701 surface tension instrument at 302 K.

2.1.3. Synthesis and characterization

The phosphines, (4-*tert*-butylphenyl)diphenylphosphine (**1**) and (4-*tert*-butylphenyl)phenylphosphine (**2**), bis-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (**3**), phenyl-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (**4**) and bis-(4-*tert*-butylphenyl)-(3-sodium sulfonatophenyl) phosphine (**5**) were obtained with multigrams scale by the method described in literature [27]. The compounds were characterized by NMR (^{1}H and ^{31}P(^{1}H)) and the data were coincided with those reported in literature [27].

The rhodium complexes based on the *tert*-butyl-substituted phosphines with the general formula *trans*-$Rh(CO)Cl(L)_2$ (L stands for the ligands of **1**, **2**, **3**, **4** and **5**, respectively) were synthesized through the reaction between 2 moles of phosphines with 1 mole of $RhCl_3$ by referring to the method described in literature [28]. All compounds are yellowish and characterized by ^{31}P(^{1}H)-NMR and IR.

2.1.4. Cone angle (θ) calculations

Gaussian98 [29] programs were used in modeling of the ligands. For geometrical optimizations at Hartree–Fock level, the 3-21G* basis set was used. Estimation of steric size of the prepared phosphine ligands was investigated by Tolman's cone angle method [30]. Cone angle determinations were done with the metal (dummy atom)–phosphorous distance, 2.28 Å, and the van der Waals radii of hydrogen, 1.2 Å.

2.2. Hydroformylation

The typical olefin hydroformylation was carried out in a stainless steel autoclave of 60 ml with a magnetic stirrer. After the rhodium complex, ligand, water, α-olefin and toluene were placed in the autoclave, the reactor was pressurized three times with 1.0 MPa of CO/H_2 (1/1, V/V). Then, the autoclave was pressurized with the same gas mixture at a desirable pressure, and heated to the reaction temperature. After the reaction, the reactor was cooled to room temperature and decompressed. Finally, the liquids and the catalysts were separated by decantation. The organic phase was analyzed with a gas chromatograph equipped with FID and a capillary column (SE-30, 30 m $\times$ 0.32 mm $\times$0.25 μm).

3. Results and discussion

3.1. Properties of free ligands

The organic-soluble phosphines, (4-*tert*-butylphenyl)-diphenylphosphine (**1**) and (4-*tert*-butylphenyl)phenyl-phosphine (**2**) were prepared by the method described in literature with high purities (close to 100%) according to the results of ^{31}P(^{1}H)-NMR [27]. Sulfonation of the organic phosphines **1** and **2** with 50% oleum could afford three water-soluble phosphines, bis-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)-phosphine (**3**), phenyl-(3-sodium sulfonatophenyl)-(4-*tert*-butyl-phenyl)-phosphine (**4**) and bis-(4-*tert*-butylphenyl)-(3-sodium sulfonatophenyl) phosphine (**5**), respectively. However, these water-soluble phosphines are generally achieved with the purities of 85–90% (^{31}P(^{1}H)-NMR) containing 10–15% impurity of oxidized phosphorus (V) species. The NMR results confirm that the *tert*-butyl group is stable under the sulfonation conditions and avoids the sulfonation of the aromatic ring bearing it. The schematic structures of ligands are presented in figure 1.

The ^{31}P(^{1}H)-NMR data and steric demands for free ligands are presented in table 1. As expected, the cone angle increases steadily because of the existence of *tert*-butyl group(s) in the *para*-position of phosphorus atom in the aromatic ring. Electronically, the organic- or water-soluble ligands should not differ much from each other or from the triphenylphosphine (PPh_3) and the

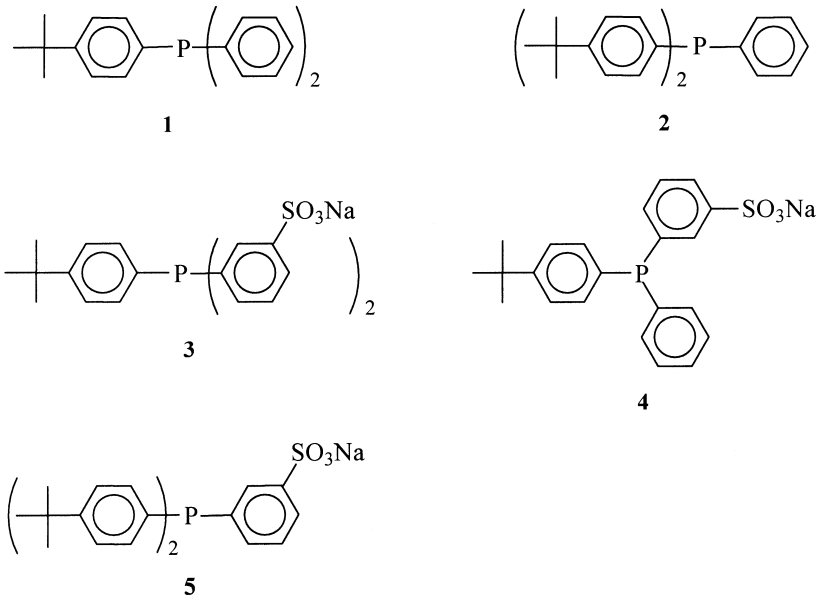

Figure 1. Schematic structures of the phosphines.

sulfonated triphenylphosphine, respectively. The role of such non-coordinating *tert*-butyl group(s) in catalysis may be to act as steering "arms" for the substrate, thus affecting the conversion and product distribution. The unsulfonated aromatic ring(s) bearing the *tert*-butyl group in the three new ligands is considered functioning as the hydrophobic group(s), which conceivably let them possess the surface-active property.

The surface tension profiles for the phosphines **3**, **4**, **5**, TPPTS and TPPDS at 302 K are shown in figure 2. It is found that in the case of **3**, **4** and **5** the surface tensions decrease linearly as a function of concentrations and then reach the minimum values with plateaus, behaving as that for the typical surfactants. The sequence of critical micelle concentrations (CMC) for **3**, **4** and **5** is CMC**3** > CMC**4** ≫CMC**5**, with the corresponding values of 2.0×10^{-2}, 1.8×10^{-3} and 2.1×10^{-5} mol L^{-1}, respectively. The surface tensions of TPPTS and TPPDS, however, keep almost constant

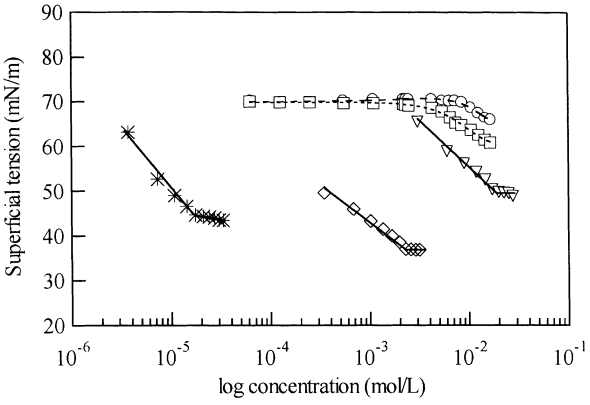

Figure 2. The surface tensions profiles of the aqueous solution of phosphines **3**, **4**, **5**, TPPTS and TPPDS at 302 K. ○: TPPTS; □: TPPDS; ▽: **3**; ◇: **4**; ∗: **5**.

and show no minimum values against the concentrations, revealing the hydrotropic property of TPPTS and TPPDS.

Table 1
Spectroscopic results for the free and the coordinated ligands

	Free ligand		$Rh(CO)Cl(L)_2$		
Ligand	Cone angle (θ)	$^{31}P(^1H)$-NMR (δ ppm)	$^{31}P(^1H)$-NMR (δ ppm)	J_{P-Rh} (Hz)	ν_{CO} (cm^{-1})
PPh_3	146	−5.03	30.06	124	1967
1	152	−6.07	28.29	125	1967
2	159	−6.11	27.18	125	1969
3	164	−6.27	30.98	123	1978
4	155	−6.65	30.52	122	1981
5	185	−12.08	30.46	122	1982
TPPDS	157	−5.81	31.26	122	1981
TPPTS	160	−5.32	31.78	125	1981

3.2. Rhodium complexes

Reaction between $RhCl_3$ and *tert*-butyl-substituted phosphines was able to afford yellowish compounds of rhodium complexes with a general formula of *trans*-$Rh(CO)Cl(L)_2$. The $^{31}P(^1H)$NMR and FTIR data for *trans*-$Rh(CO)Cl(L)_2$ are incorporated in table 1. It is known that the coupling constant J_{P-Rh} describes the property of a particular P–M bond and is a useful parameter for estimating the electron donor/acceptor properties of the coordinated ligands [31]. Additionally, the carbonyl stretching frequency is relatively free of steric effects and thus reflects the electronic state of the bound phosphine ligand [30,32]. The values of IR stretching frequencies (1944–1981 cm^{-1}) and coupling constants (123–127 Hz) for the *trans*-$Rh(CO)Cl(L)_2$ species in table 1 suggest that the ligands are electronically similar to each other and not much different from the triphenylphosphine analogs, whereas the higher values of $\nu(CO)$ for the water-soluble phosphine-rhodium complexes than those for the organic-soluble ones are ascribed to the electronic withdrawing effect of the sulfonate group(s).

3.3. Catalytic studies

To investigate the steric effect of *tert*-butyl-substituted phosphines **1** and **2** on the regio-selectivity of hydroformylation products, we conducted the 1-hexene hydroformylation with homogeneous rhodium system at temperature of 373 K by using **1**, **2** and PPh_3 as ligands, respectively. The conversion was controlled roughly to a same level as listed in table 2. Here, the 100% conversion of 1-hexene corresponds to a reaction rate of 7.5×10^4 mol h^{-1} mol–Rh^{-1}. The data reveal that the complex with phosphines **1** and **2** bearing the bulk *tert*-butyl group(s) even in the *para*-position of phosphorus atom has advantages over PPh_3 in the product selectivity toward the normal heptanal, probably owing to the larger cone angle of the ligands.

Table 3 lists the hydroformylation results of 1-hexene, 1-octene and 1-dodecene with aqueous biphasic catalysis system using $Rh(acac)(CO)_2$ as catalyst precursor and water-soluble phosphines **3**, **4**, **5**, TPPTS and TPPDS as ligands, respectively. All the reactions were carried out under the same conditions under $L/Rh = 10$ (mol/mol^{-1}) and olefin/$Rh = 2500$

Table 2
Effects of ligands on 1-hexene hydroformylation in homogeneous rhodium system

Ligand	Cone angle (θ)	Conversion (%)	TOF (h^{-1})	STY (mmol h^{-1} g_{-Rh}^{-1})	n/i
1	152	44.5	3.01×10^4	2.92×10^5	3.4
2	159	45.0	3.34×10^4	3.24×10^5	4.0
PPh_3	146	40.1	3.38×10^4	3.28×10^5	2.3

Note: Reaction conditions: [Rh] = 0.0064 mmol, 1-hexene/Rh = 2500 (mol mol^{-1}), $CO/H_2 = 1$ (V/V), $L/Rh = 10$ (mol mol^{-1}), T = 373 K, $P_{(CO/H_2)} = 1.5$ MPa, 1-hexene = 2 ml, toluene = 5 ml, reaction time = 2 min.

Table 3
Effects of ligands on the higher olefin hydroformylation in biphasic system

Olefin	Ligand	Conversion (%)	n/i	TOF (h^{-1})	STY (mmol h^{-1} g_{-Rh}^{-1})
	3	46.4	4.4	290.0	2818.3
	4	72.8	2.5	445.0	4324.6
1-hexene	**5**	70.8	6.4	442.5	4300.3
	TPPDS	18.8	3.1	117.5	1141.9
	TPPTS	15.4	4.1	96.3	935.9
	3	55.8	5.4	348.8	3389.7
	4	78.9	3.2	493.1	4792.0
1-octene	**5**	74.7	7.0	466.9	4537.4
	TPPDS	9.5	3.7	59.4	577.3
	TPPTS	3.5	5.3	21.9	212.8
	3	65.3	6.7	408.1	3966.0
	4	85.1	4.4	531.9	5169.1
1-dodecene	**5**	14.7	8.0	91.9	893.1
	TPPDS	7.8	4.3	48.8	474.2
	TPPTS	0.0	0.0	0.0	0.0

Note: Reaction conditions: Olefin/Rh = 2500 (mol mol^{-1}), CO/H_2 (V/V) = 1, T = 373 K, $P_{(CO/H_2)} = 1.5$ MPa, reaction time = 4 h, agitation speed = 800 rpm, water/organic = 3 : 1, $L/Rh = 10$ (mol mol^{-1}).

(mol/mol^{-1}). The 100% conversion of olefin corresponds to a reaction rate of 625 mol/h^{-1} mol–Rh^{-1}. As for TPPDS and TPPTS, the longer the chain length of the olefin, the lower the reaction rate achieved. The 1-dodecene that has the longest chain cannot be hydroformated with the Rh–TPPTS system due to the high hydrophilicity of TPPTS, but slightly converted to the corresponding aldehyde with Rh–TPPDS in which the TPPDS contains a hydrophobic group of aromatic ring. On the other hand, the use of **3**, **4** and **5** allows obtaining higher reaction rates, since the different density and molecular mass of the substrates, the L/Rh ratio of 10 in the reaction system of 1-hexene, 1-octene and 1-dodecene corresponds to the phosphine concentrations of 7.1×10^{-3}, 6.3×10^{-3} and 4.8×10^{-3} mol L^{-1}, respectively. Thus, though the CMC of surfactant may drop slightly in the reaction media, the L/Rh ratio of 10 in the case of phosphine **3** means that the phosphine concentration is lower than its CMC, while, as for the phosphines **4** and **5**, the studies are done at concentrations that exceed well above their CMCs. The variable reaction rates obtained with the catalysts based on **3**, **4** and **5** suggest that the complicated effects arise from the amphiphilic phosphines.

Plots of conversion and aldehyde n/i ratio *versus* the L/Rh mole ratio in the 1-dodecene hydroformylation by using amphiphilic phosphines **3**, **4** and **5** as ligands are shown in figure 3, respectively. The phosphine concentration with respect to L/Rh ratio is also provided in figure 3. Herein, the 100% conversion of 1-dodecene corresponds to a reaction rate of 625 mol h^{-1} mol–Rh^{-1}. It is found that the reaction rate goes through a maximum with increase of L/Rh ratio at around the CMC of the phosphines **4** and **5** and then drops. The maximum reaction rate in the case of the catalyst generated from the phosphine **3**, however, appears in the phosphine concentration lower than its CMC. The result is probably due to the higher hydrotropic property of **3** and thus relatively less surface-activity, as reflected by its higher value of CMC. It is typical for the surfactant like CTAB that at the concentration higher than CMC, the advantage of activity acceleration is diminished and the hydroformylation selectivity is lost [9]. However, in contrast with the system of CTAB addition, the values of n/i ratio keep increasing with the L/Rh ratio in the present studies. The results indicate that the phosphines **3**, **4** and **5** function as typical surfactants and typical phopshine ligands simultaneously during the olefin hydroformylation. Furthermore, the curves obtained in figure 3 account well for the variable data in table 3.

Figure 4 depicts the reaction conversion and n/i ratio of 1-hexene hydroformylation in a biphasic rhodium complex system as a function of L/Rh by using **3**, **4**, **5,** TPPTS and TPPDS as ligands, respectively. The phosphine concentration with respect to L/Rh ratio is provided in the figure. Here, the 100% conversion of 1-hexene corresponds to a reaction rate of

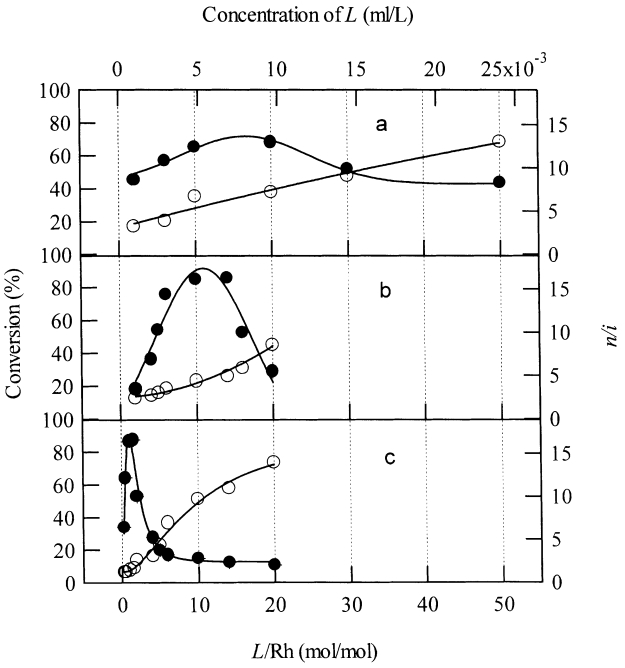

Figure 3. The conversion and n/i ratio in the hydroformylation of 1-dodecene as a function of L/Rh and phosphorous concentration by using (a) **3**, (b) **4** and (c) **5** as ligands. The CMC for **3**, **4** and **5** is 2.0×10^{-2}, 1.8×10^{-3} and 2.1×10^{-5} mol L^{-1}, respectively. Reaction conditions: [Rh] = 4.0×10^{-3} mol L^{-1}, others are the same as in table 3. ●: conversion; ○: n/i ratio.

625 mol h^{-1} mol–Rh^{-1}. In the case of TPPTS and TPPDS as ligands, the reaction conversion increases slightly to reach a maximum value and then decreases with increasing L/Rh ratio, whereas the n/i ratio of heptanal keeps increasing throughout the experiment. With the use of amphiphilic phosphines **3**, **4** and **5** as ligands, however, the enhancements both in the reaction rate and the n/i ratio of heptanal are obtained. The maximal catalytic activities of the rhodium complexes with **3**, **4** and **5** for the hydroformylation of 1-hexene are about 3.1, 4.9 and 4.8 times higher than that of TPPTS–Rh, and also about 2.5, 4.0 and 3.9 times higher than that of TPPDS–Rh, respectively. The variations of reaction rate against the L/Rh ratio employed as shown in figure 4 are similar to those in figure 3, but the curves go more smoothly, probably due, in part, to the slight water solubility of 1-hexene.

The above results suggest that the micelles may be formed spontaneously in the aqueous solution while using the catalysts generated from the amphiphilic phosphines **3**, **4** and **5** for the hydroformylation of longer chain olefins, respectively. The aggregates formed due to the amphiphilic phosphines **3**, **4**, **5** and their corresponding rhodium complexes have pronounced effect on the solubility of organic substrates. Thus, the catalysts show not only a higher catalytic activity but also a higher selectivity to normal aldehdyes in comparison with ligands that do not form aggregates. The drop in the catalytic activity may be partially due to

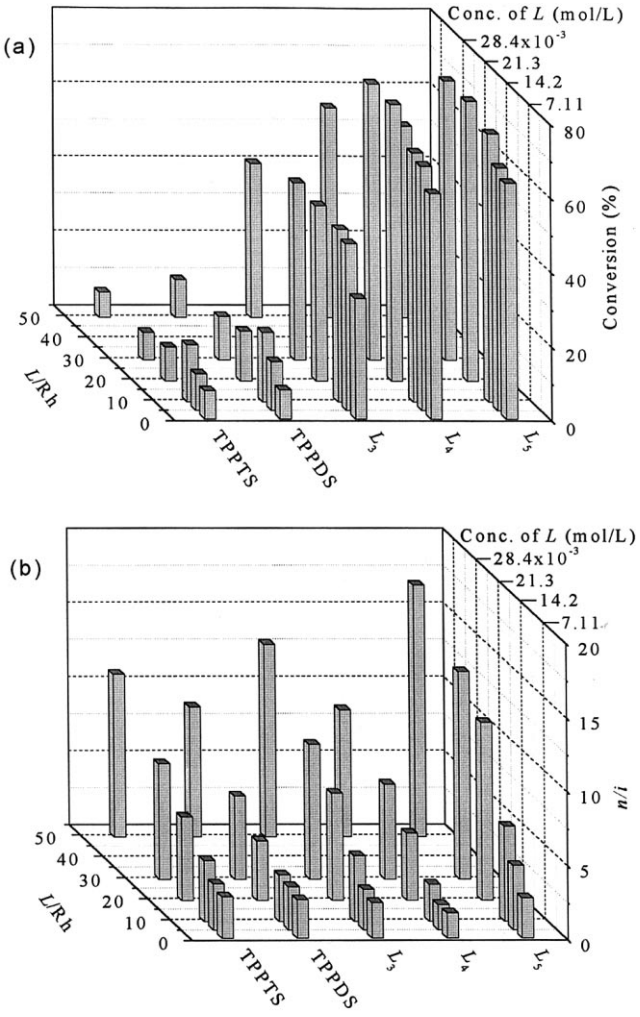

Figure 4. The reaction profiles for the hydroformylation of 1-hexene as a function of L/Rh by using **3**, **4**, **5**, TPPDS and TPPTS as ligands. Reaction conditions: [Rh] = 5.3×10^{-3} mol L^{-1}, others are the same as in table 3. (a) conversion and (b) n/i ratio.

the inaccessibility of the rhodium at high concentration of the amphiphilic phosphines when the vesicles are formed.

The recycling of the catalysts based on these amphiphilic phosphines was examined by performing a series of consecutive runs. The results are shown in figure 3. The catalyst based on phosphine **5** loses its original activity and selectivity gradually from the first to sixth run, indicating that the high activity observed with this phosphine is mainly due to the presence of catalyst in the organic phase. A slight decrease of less than 5% in the catalytic activity is observed between each run from the first to the fourth run, and then it drops quickly with the phosphine **4**, while the selectivity to normal aldehyde keeps almost stable throughout the six runs. The results suggest that this phosphine does not retain rhodium quantitatively in the aqueous phase. Attractively, the catalyst generated from the phosphine **3** can be recovered for at least six times without

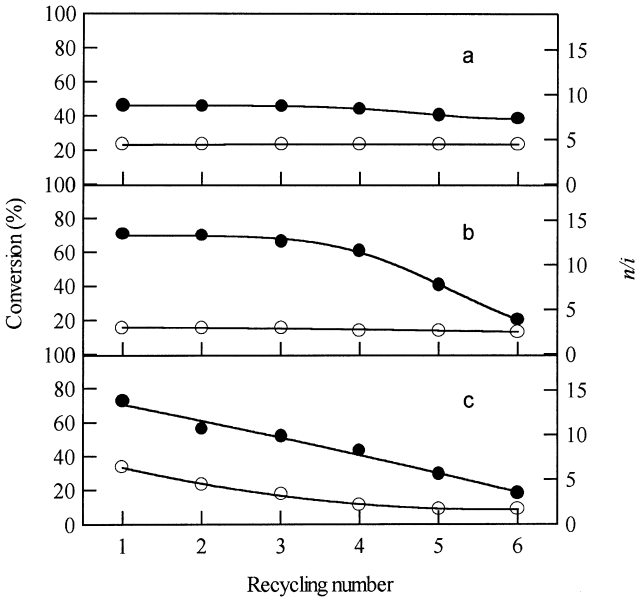

Figure 5. Comparison of catalyst recycling in the hydroformylation of 1-hexene by catalysts based on (a) **3**, (b) **4** and (c) **5**. Reaction conditions are the same as in figure 4. ●: conversion; ○: n/i ratio.

significant loss in the catalytic performances. Furthermore, the experiments prove that the phase separation is easy and there is no formation of emulsions.

4. Conclusions

(1) The new series of amphiphilic phosphines **3**, **4** and **5** bearing the *tert*-butyl group(s) in the aromatic ring(s) are electronically similar to each other and similar to the sulfonated triphenylphosphines, TPPTS and TPPDS, but the steric demand of *tert*-butyl group(s) cause phosphines **3**, **4** and **5** to possess larger cone angles.

(2) When **3**, **4** and **5** are used in the aqueous biphasic rhodium complex systems for the hydroformylation of higher olefins of 1-hexene, 1-octene and 1-dodecene, they behave as typical surfactant and ligand simultaneously. The catalysts thus allow hydroformylating higher olefin to produce corresponding aldehyde under mild conditions.

(3) The phosphines **3**, **4**, **5** and their corresponding rhodium complexes form aggregates in the water phase, which have beneficial effect on the solubility of organic substrates. A higher activity along with a higher selectivity to normal aldehdye can be achieved with the proper L/Rh ratio.

(4) The best catalytic activity of rhodium complexes with **3**, **4** and **5** for the hydroformylation of 1-hexene are about 3.1, 4.9 and 4.8 times higher than that of TPPTS–Rh, and also about 2.5, 4.0 and 3.9 times higher than that of TPPDS–Rh, respectively.

(5) No significant loss in the catalytic performances has been observed with the catalyst generated from the

phosphine **3** for six times. The amphiphilic phosphine is unique in aqueous phase catalysis since the formation of micelles is spontaneous and the catalytically active aggregates allow an easy separation of the product and the catalyst. The phosphine **3** may fulfill the requirements for aqueous biphasic hydroformylation of higher olefins.

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