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Amphiphilic phosphines for catalysis in the aqueous phase

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Abstract

Two new phosphines, Tris[*p*-(10-phenyldecyl)phenyl]phosphine and 2,2′-Bis{di[*p*-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl were successfully synthesized and sulfonated in concentrated H_2SO_4. The resulting water soluble surface active phosphines were applied to the rhodium catalyzed hydroformylation of higher olefins. It is found that these two ligands are not only excellent for octene hydroformylation, but catalyze tetradecene hydroformylation under two phase conditions as well. Rates and selectivities are superior to TPPTS modified rhodium catalysts under the same reaction conditions.

1. Introduction

One of the major problems of homogeneous catalysis for industrial applications is the separation of catalyst from product [1]. A viable method for separation must be developed before a new homogeneous catalyst is commercialized. Since the lifetime of a catalyst in an industrial process is greatly affected by the means of separation, the more efficient the separation the longer catalyst life. The use of water soluble catalysts is an effective means of catalyst immobilization and leads to very efficient separations.

The introduction of the Ruhrchemie/Rhone Poulenc process for rhodium catalyzed hydroformylation of propene with trisulfonated triphenylphosphine, TPPTS, allows the recycle of catalysts by a simple phase separation [2]. Unlike catalysis in organic solvents, the water soluble catalysts operate under two phase reaction conditions and can be easily recovered due to their immiscibility with the organic products. The long lifetime of the expensive rhodium catalyst reduces the operational cost of Ruhrchemie/Rhone Poulenc process [3]. This along with beneficial environmental effects, e.g. fewer emissions of volatile organic solvents compared to similar processes in organic solvents, make the aqueous-phase process very desirable [3,4]. In turn, the design and synthesis of new water soluble phosphines for aqueous-phase catalysis has been attracted a great deal of attention due to the success of the Ruhrchemie/Rhone Poulenc process [5].

However, the reactivity of the water soluble catalyst is somewhat limited by the solubility of the organic substrate in aqueous phase. Thus, the application of TPPTS based catalysts is limited to substrates that have appreciable water solubility. Recently, we introduced a number of novel water soluble phosphines which are surface active, such as $P[(C_6H_4(CH_2)_x\text{-}p\text{–}C_6H_4\text{–}SO_3Na]_3$, x=3, 6, [6] and chelating phosphines bearing the sulfonated pendants -$[(C_6H_4(CH_2)_x\text{-}p\text{–}C_6H_4\text{–}SO_3Na]$ [7]. Catalytic results from the two phase hydroformylation of 1-octene with rhodium

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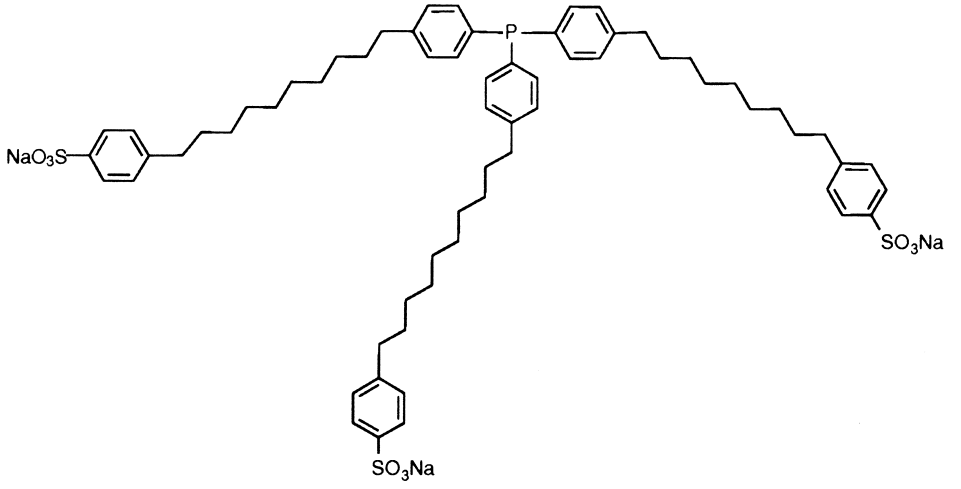
complexes of these phosphines show improved catalytic activity and selectivity compared to the Rh/TPPTS system. The improved reaction rates may be due to the surface activity of these phosphines which increases the mixing of the catalyst and substrate phases. Indeed, it was shown that catalytic activity increases as ligand aggregation becomes more likely.

In order to further exploit the benefits brought by the surface activity of such phosphines, two new phosphines with even longer pendants, tris[*p*-(10-*p*-sulfonatophenyl-decyl)phenyl]phosphine, **1**, and the chelating phosphine tetrasulfonated 2,2′-bis{di[*p*-(10-phenyldecyl)-phenylphosphinomethyl}-1,1′-biphenyl **2** have been synthesized. These two phosphines give higher activity towards hydroformylation of 1-octene



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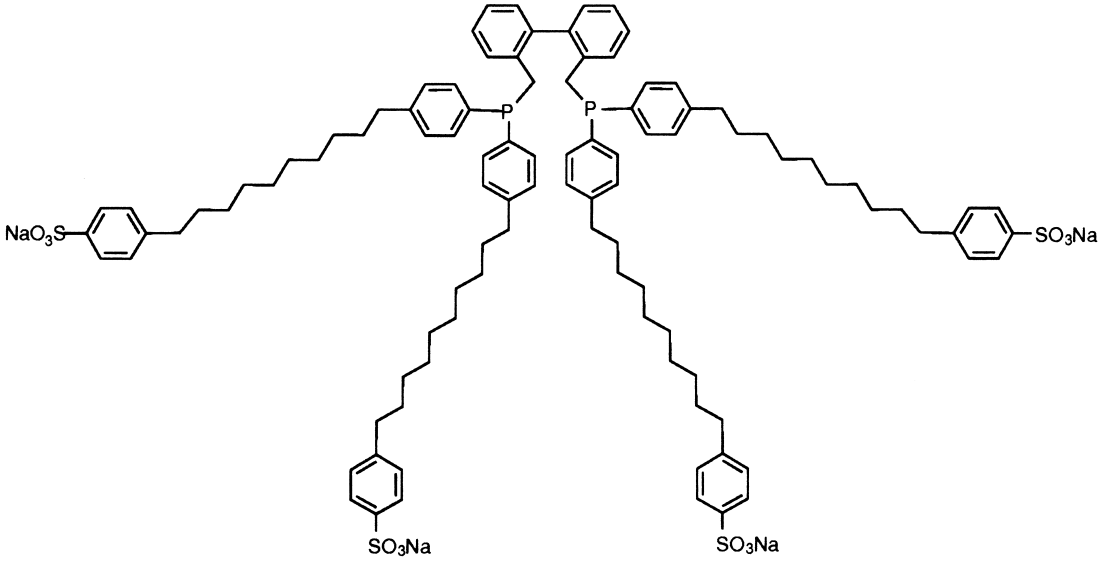

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Scheme 1.

under two phase conditions, but also enable the hydroformylation of longer chain olefins, such as 1-tetradecene Scheme 1.

2. Experimental section

All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. All nonaqueous solvents used in the reactions were dried by usual means and distilled under argon prior to use. House distilled water was redistilled in an all glass distillation flask under argon.

Routine NMR measurements were done on a Bruker WP 200 at an observation frequency of 200.133 MHz for ^{1}H; 50.323 MHz for ^{13}C; and 81.015 MHz for ^{31}P. Some high field ^{1}H,^{13}C,^{31}P NMR data were obtained on a Varian RU400 NMR spectrometer at 399.052, 100.577, 161.903 MHz, respectively. Key to NMR data: s, singlet; d, doublet; t, triplet; quart, quartet; quin, quintet; m, multiplet; br, broad; asterisk, pseudo.

2.1. The synthesis of Tris[p-(10-p-sulfonatophenyldecyl)phenyl]phosphine **1**

2.1.1. The synthesis of 10-bromo-1-phenyl-decane

1,10-dibromodecane (100 g, 0.33 mol) and diethylether (100 ml) were placed in a 500 ml three-neck flask equipped with a gas inlet, an equal-pressure dropping funnel and a reflux condenser. The solution was chilled with an ice-water bath. Phenyllithium (100 ml, 1.8 M, 0.18 mol in cyclohexane-ether) was added dropwise over 2 h. The ice-water bath was removed and the reaction mixture was heated to reflux for 36 h to give a pale-yellow solution with a white precipitate. The mixture was filtered and the solvent was removed under reduced pressure. The resulting yellow oil was then distilled under vacuum. 10-bromo-1-phenyl-decane, 20.4 g, was recovered from the distillation at 148–152°C (1 torr) as a colorless liquid (37% yield based on phenyllithium). ^{1}H NMR (δ in $CDCl_3$): 1.28 (br.s., 10 H); 1.38 (m, 2H); 1.61 (*quin, $^{3}J_{H-H} = 7.0$Hz, 2H); 2.60 (t, $^{3}J_{H-H} = 7.7$Hz, 2H); 3.39 (t, $^{3}J_{H-H} = 6.9$ Hz, 2H); 7.1-7.3 (m, 5H). ^{13}C NMR (δ in $CDCl_3$): 28.15 (s, 1C); 28.73 (s, 1C); 29.27 (s, 1C); 29.39 (s, 1C); 29.43 (s, 2C); 31.46 (s, 1C); 32.83 (s, 1C); 33.94 (s, 1C); 35.95 (s, 1C); 125.54 (s, 1C); 128.19 (s, 2C); 128.37 (s, 2C); 142.87 (s, 1C). MS: 298 (M^{+})

2.1.2. The synthesis of 4-(10-phenyldecyl)-1-chlorobenzene

1-bromo-4-chlorobenzene (14.0 g, 0.073 mol) in 100 ml diethylether was introduced into a 250 ml three-neck flask equipped with a gas inlet, two equal-pressure dropping funnels. The solution was chilled with an ice-water bath. *n*-Butyllithum (46 ml, 1.6 M in hexanes) was added from the first dropping funnel. The addition was completed in 15 min and immediately 10-bromo-1-phenyl-decane (20 g, 0.067 mol) in 20 ml diethyl ether was introduced over a 10 min period from the second dropping funnel. The ice-water bath was removed and the mixture was allowed to warm up to room temperature. One dropping funnel was replaced with a condenser and the reaction mixture was refluxed for 72 h. The resulting yellow solution with white precipitate was filtered and the solvent was removed from filtrate under reduced pressure. The product, 4-(10-phenyldecyl)-1-chlorobenzene, was purified by vacuum distillation in 26% of yield (5.7 g, colorless oil, bp: 190–195°C at 1 torr.). ^{1}H NMR (δ in $CDCl_3$): 1.27 (br.s., 6 H); 1.28 (br.s., 6 H); 1.57 (m, 4H); 2.57 (m, 4H); 7.0–7.3 (m, 9H). ^{13}C NMR (δ in $CDCl_3$): 29.15 (s, 1C); 29.30 (s, 1C); 29.42 (s, 1C); 29.46 (s, 1C); 29.52 (s, 2C); 31.34 (s, 1C); 31.48 (s, 1C); 35.27 (s, 1C); 35.97 (s, 1C); 125.53 (s, 1C); 128.19 (s, 2C); 128.23 (s, 2C); 128.32 (s, 2C); 129.70 (s, 2C); 131.50 (s, 1C); 141.29 (s, 1C); 142.91 (s, 1C);. MS: 328 (M^{+})

2.1.3. The synthesis of Tris[p-(10-phenyldecyl)phenyl]phosphine

4-(10-phenyldecyl)-1-chlorobenzene (2.4 g, 7.3 mmol) in 50 ml diethylether/THF (50/50) was placed in a 100 ml side-armed flask under argon with an ice-water bath. Lithium (0.10 g, 14.6 mmol) was chopped directly into the flask. The solution turned red in 2 min. The ice-water bath was removed and the mixture was stirred for an additional 4 h. The resulting deep-red solution was filtered to remove LiCl. The solution was chilled with an ice-water bath and PCl_3 (0.33 g, 2.4 mmol) in 10 ml diethyl ether was added dropwise from an equal-pressure dropping funnel. The addition was finished in 15 min and the mixture was

stirred overnight. A pale-yellow solution with precipitate resulted. The solvents were removed under reduced pressure and replaced with 50 ml diethyl ether. The mixture was then filtered and the ether solution was further washed twice with 10 ml water and dried over $MgSO_4$. The ether was then removed and the final product, a yellow oil at room temperature, was further purified by recrystallization with 50 ml pentane at −78°C. Tris[*p*-(10-phenyldecyl)phenyl]-phosphine, a pale-yellow oil, was recovered in 75% yield (1.64 g). ^{1}H NMR (δ in $CDCl_3$): 1.26 (br.s, 18 H); 1.29 (br.s., 18 H); 1.59 (m, 12H); 2.58 (*quart, 12H); 7.10–7.30 (m, 27H). ^{13}C NMR (δ in $CDCl_3$): 29.33 (s, 3C); 29.37 (s, 3C); 29.48 (s, 3C); 29.50 (s, 3C); 29.55 (s, 3C); 29.56 (s, 3C); 31.32 (s, 3C); 31.53 (s, 3C); 35.79 (s, 3C); 35.99 (s, 3C); 125.53 (s, 3C); 128.20 (s, 6C); 128.38 (s, 6C); 128.53 (d, $^3J_{C-P}$ =7.2 Hz, 6C); 133.63 (d, $^2J_{C-P}$ =19.8 Hz, 6C); 134.38 (d, $^1J_{C-P}$ =9.6 Hz, 3C); 142.93 (s, 3C); 143.49 (s, 3C). ^{31}P NMR (δ in $CDCl_3$): −7.1 (s). MS: 926 (M^+ as oxide).

2.1.4. *The synthesis of Tris[p-(10-p-sulfonatophenyldecyl)phenyl]phosphine* **1**

Tris[*p*-(10-phenyldecyl)phenyl]phosphine (1.6 g, 1.8 mmol), was dissolved in 8 ml H_2SO_4 (96%) with an ice-water bath. The brown solution was stirred at room temperature for 6 h. The mixture was then neutralized by 20% (w/w) aqueous NaOH. The final pH was 8.5. 300 ml of methanol was added and the mixture was brought to reflux for 30 min. The precipitate, Na_2SO_4, was then filtered and the salt was washed with 100 ml hot methanol. Two portions of the solution were combined and the volume was reduced to 10 ml. 100 ml of acetone was then added to generate a white precipitate. The precipitate, Tris[*p*-(10-*p*-sulfonatophenyldecyl)phenyl]phosphine **1**, was collected by filtration and dried under vacuum (1.75 g, 82% yield). ^{1}H NMR (δ in CD_3OD): 1.27 (br.s, 18 H); 1.30 (br.s., 18 H); 1.60 (m, 12H); 2.60 (m, 12H); 7.14 (br.*d, 12H); 7.22 (*d, 6H); 7.72 (*d, 6H). ^{13}C NMR (δ in CD_3OD): 30.32 (s, 3C); 30.37 (s, 3C); 30.54 (s, 3C); 30.57 (s, 3C); 30.67 (s, 6C); 32.57 (s, 6C); 36.67 (s, 3C); 36.70 (s, 3C); 126.99 (s, 6C); 129.25 (s, 6C); 129.65 (d, $^3J_{C-P}$ = 6.8 Hz, 6C); 134.67 (d, $^2J_{C-P}$ = 19.8Hz, 6C); 135.82 (d, $^1J_{C-P}$ = 11.5 Hz, 3C); 143.72 (s, 3C); 144.89 (s, 3C); 146.64 (s, 3C). ^{31}P NMR (δ in CD_3OD): -6.2 (s). MS: 1233 (M^++1 as oxide).

3. Synthesis of tetrasulfonated 2,2′-Bis{di[*p*-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl, 2

3.1. *The synthesis of Di [p-(10-phenyldecyl)phenyl]chlorophosphine*

p-(10-phenyldecyl)phenyllithium (8.0 mmol), generated from the lithiation of 4-(10-phenyldecyl)-1-chlorobenzene (2.63 g, 8.0 mmol) in 50 ml solvent (Et_2O/THF 1/1) as described previously, was added dropwise to CH_3OPCl_2 (0.53 g, 4.0 mmol) in 15 ml solvent (Et_2O/THF 1/1) at −70°C. The addition was completed in 1 h. The reaction mixture was stirred overnight at room temperature. The precipitate was filtered and the solvent was removed at reduced pressure. PCl_3 (9 ml) was added to the resulting viscous oil and stirred for 24 h. Then the mixture was kept at 70°C and 1 mm Hg for 2 h to remove excess PCl_3 and byproduct. The product, di[*p*-(3-phenylpropyl)phenyl]chlorophosphine, was obtained as a pale- yellow viscous oil quantitative yield. ^{31}P NMR (δ in $CDCl_3$): 81.1 (s).

3.2. *The synthesis of 2,2′-Bis{di[p-(10-phenyldecyl)phenyl]phosphinomethyl}-1,1′-biphenyl*

Di[*p*-(10-phenyldecyl)phenyl]chlorophosphine (2.55 g, 4.0 mmol) was dissolved in 60 ml THF and Li (0.056 g, 8.0 mmol) was chopped directly into the reaction flask under Ar. A deep red solution resulted in 10 min and all the lithium was consumed in 5 h. The solution was then filtered and 2,2′-dibromomethyl-1,1′-biphenyl (0.68 g, 2.0 mmol) in 20 ml THF was added dropwise with an ice-water bath. The color of the solution slowly changed to pale- yellow. The mixture was stirred for additional 10 h before the solvent was removed by vacuum. 50 ml diethyl ether was added and it was washed with 3×20 ml H_2O. The ether phase was dried over $MgSO_4$ and the solvent was then removed by vacuum. The resulting pale- yellow viscous oil was further purified by recrystallization with 50 ml pentane at −78°C. 1.5 g (54% yield) of 2,2′-Bis{di[*p*-(10-phenyldecyl)phenyl]phosphinomethyl}-1,1′-biphenyl was recovered as a pale-yellow

oil. ^{1}H NMR (δ in $CDCl_3$): 1.26 (br. s, 24H); 1.29 (br.s, 24H); 1.59 (m, 16H); 2.53 (t, $^3J_{H-H}$ =6.1 Hz, 8H); 2.59 (t, $^3J_{H-H}$ =7.7 Hz, 8H); 3.12 (*quart, 4H); 6.9–7.4 (m, 44H). ^{13}C NMR (δ in $CDCl_3$): 29.31 (s, 4C); 29.35 (s, 4C); 29.48 (br.s, 8C); 29.56 (br.s, 8C); 31.33 (d, $^1J_{c-p}$=7.6 Hz, 2C); 31.51 (br.s, 8C); 35.73 (s, 4C); 35.97 (s, 4C); 125.50 (s, 4C); 126.95 (s, 2C); 128.17 (s, 8C); 128.35 (s, 8C), 129.73 (d, $^3J_{c-p}$=10.0 Hz, 2C); 130.38 (s, 2C); 132.60 (d, $^3J_{c-p}$=19.1 Hz, 8C); 133.17 (d, $^2J_{c-p}$=19.8 Hz, 8C); 134.97 (d, $^1J_{c-p}$=14.6 Hz, 4C); 135.31(s, 2C); 135.96 (d, $^3J_{c-p}$=8.3 Hz, 2C); 140.86 (d, $^2J_{c-p}$=3.8 Hz, 2C); 142.88 (s, 4C); 143.10 (s, 4C). ^{31}P NMR (δ in $CDCl_3$): −14.1 (s). Mass Spectrometry (FAB, on phosphine oxide): 1447 (M^++1)

3.3. *Synthesis of tetrasulfonated 2,2′-Bis{di[p-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl,* **2**

2,2′-Bis{di[*p*-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl (1.3 g, 0.9 mmol), was dissolved in 8 ml H_2SO_4 (96%) with an ice-water bath. The brown solution was stirred at room temperature for 7 h. The mixture was then neutralized by 20% (w/w) aqueous NaOH. The final pH was 8.0. 300 ml of methanol was added and the mixture was brought to reflux for 30 min. The precipitate, Na_2SO_4, was then filtered and the salt was washed with 100 ml hot methanol. Two portions of the solution were combined and the volume was reduced to 10 ml. 70 ml of acetone was then added to generate a white precipitate. The precipitate, sulfonated 2,2′-Bis{di[*p*-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl, was collected by filtration and dried under vacuum (1.1 g, 67% yield). ^{1}H NMR (δ in CD_3OD): 1.30 (br. s, 48H); 1.59 (m, 16H); 2.55 (t, $^3J_{H-H}$ =6.7 Hz, 8H); 2.61 (t, $^3J_{H-H}$ =8.2 Hz, 8H); 3.05 (*quart, 4H); 6.8-7.8 (m, 40H). ^{13}C NMR (δ in CD_3OD): 30.35 (br.s, 8C); 30.61 (br.s, 8C); 30.73 (br.s, 8C); 32.62 (br.s, 8C); 34.27 (d, $^1J_{c-p}$=13.3 Hz, 2C); 36.68 (br.s, 8C); 126.99 (s, 8C); 129.26 (br.s, 16C), 129.38 (s, 4C); 129.55 (s, 4C); 131.28 (s, 2C); 131.53 (s, 2C); 133.63 (d, $^3J_{c-p}$=18.3 Hz, 8C); 134.45 (d, $^2J_{c-p}$=19.8 Hz, 8C); 143.71 (s, 4C); 146.65 (s, 4C). ^{31}PNMR (δ in CD_3OD): −12.3 (s). Mass Spectrometry (FAB, a glycerol matrix) 1845 (M^++Na)

4. Two phase hydroformylation with rhodium catalysts of 1 and 2

Two phase hydroformylation of high olefins (octene-1 and tetradecene-1) with Tris[*p*-(10-*p*-sulfonatophenyldecyl)phenyl]phosphine **1** and tetrasulfonated 2,2′-Bis{di[*p*-(10-phenyldecyl)phenylphosphinomethyl}-1,1′-biphenyl **2** was carried out in a 30 ml stainless steel reaction vessel. The catalyst was made in situ by mixing 0.76 ml 0.01 M Rh(acac)$(CO)_2$ in methanol and the required amount of 0.1 M aqueous solution of water soluble ligand. Water was added to adjust the total aqueous methanol volume to 1.56 ml. The substrate, 0.60 ml of 1-octene, or 0.96 ml of 1-tetradecene, was then transferred into the reaction vessel under positive pressure of CO. Nonane, 0.40 ml, was added as an internal standard for gas chromatography analysis. Therefore, the volume of organic phase is 1.0 ml for 1-octene and 1.36 ml for 1-tetradecene. The Octene/Rh ratio was 500/1 in all catalytic runs. After the reaction vessel was loaded and pressurized with CO/H_2 to 210 psi, the reaction was initiated by placing the reaction vessel into a temperature bath preheated to 120°C. The temperature of the oil bath was controlled by an Omega CN 2000 temperature process controller. The reaction mixture was constantly stirred with a magnetic stir bar at 350 rpm. Catalytic reactions were terminated by removing the vessel from the oil bath and depressurizing when it had been cooled in an ice-water bath. In all cases the organic layer was colorless and readily separated from aqueous layer after the reaction.

The reaction product distribution was analyzed by gas chromatography on a Varian 3300 gas chromatograph equipped with a HP1 column 25 m× 0.32 mm×0.52 μm, and FID detector, He was the carrier gas; the temperature program was from 40°C (4 min) to 220°C (1 min), at a heating rate of 10°C/min.

5. Results and discussion

The results obtained for octene hydroformylation with rhodium catalysts of **1** and **2** are summarized in Tables 1 and 2, respectively. The rhodium concentration is always 0.0049 M, while the ligand concentra-

Table 1
Two-phase hydroformylation of 1-octene ligand to Rh ratio variation study (**1** vs. TPPTS)

L/Rh	**1**			TPPTS		
	Yield of nonanals (%)	TOF (h^{-1})	% 1-nonanal	Yield of nonanals (%)	TOF (h^{-1})	% 1-nonanal
2	38	190	71	14	70	69
3	51	255	78	17	85	72
5	80	400	82	29	145	76
7	85	425	88	41	205	77
9	87	435	89	44	220	78

Reaction conditions: reaction time, 1 h; reaction temperature, 120°C; initial pressure, 210 psi (at 25°C); stirring rate is 350 rpm; [Rh] =0.0049 M.

Table 2
Two-phase hydroformylation of 1-octene ligand to Rh ratio variation study (**2** vs. TPPTS)

Ligand/Rh	**2**		TPPTS	
	Yield of nonanals (%)	% 1-nonanal	Yield of nonanals (%)	% 1-nonanal
2	63	65	36	68
3	76	71	45	70
5	76	79	57	75
7	80	85	57	76
9	83	91	76	76

Reaction conditions: reaction time, 5 h; reaction temperature, 120°C; initial pressure, 210 psi (at 25°C); stirring rate is 350 rpm; [Rh] =0.0049 M.

tion is systematically varied in order to observe the influence of ligand to rhodium ratio on the reaction activity and selectivity. For comparison, the TPPTS ligand was tested under the same reaction conditions. These results are also reported in Table 1 and Table 2.

The activity of the rhodium catalysts modified by **1** is quite remarkable for a water soluble triaryl phosphine. A reaction time of only one hour was used for the hydroformylation of 1-octene in a two- phase reaction with the catalyst phase of aqueous methanol. This is quite fast compared to reactions in our lab under similar conditions with simple magnetic stirring. Up to 450 turnovers are observed with **1** compared to 220 for TPPTS under the same at a L/Rh ratio of 9. At all L/Rh ratios investigated **1** showed superior activity compared to TPPTS. The ligand also yields the most active catalyst for all the phosphines in the series, $P[(C_6H_4(CH_2)_x\text{-}p\text{-}C_6H_4\text{-}SO_3Na]_3$, x=3, 6, 10. Previously, it was argued that the improved activity of the amphiphilic ligands of this type is due to improved transfer of the substrate to the aqueous phase in the presence of phosphines which are able to aggregate into small micelles. This effect appears to be further enhanced as the number of methylene groups increases to ten in **1**.

The use of aqueous methanol as the reaction medium for TPPTS hydroformylation catalysts is well known to improve reaction rates and to decrease hydroformylation selectivity significantly [8]. In water alone as the solvent conversions are very low with TPPTS based catalysts [9]. The phases separate completely and the nonaqueous phase shows no residual activity for the hydroformylation reaction, thus the aqueous methanol reaction medium is suitable for biphasic catalysis. With amphiphilic phosphines the tendency to lower reaction selectivity in methanol is diminished [6,9]. The improved selectivity with amphiphilic phosphines compared to TPPTS in aqueous methanol is attributed to decreased intra-complex ionic repulsions between sulfonate groups in the reaction intermediates. For example in the presumed

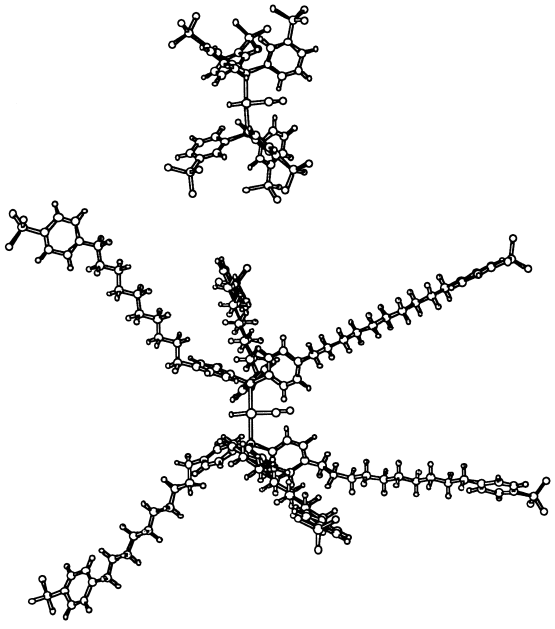

Fig. 1. CACHE drawings of the complexes HRh(**1**)$_2$(CO) (bottom), and HRh(TPPTS)$_2$(CO) (top).

intermediates, HRh(1)$_2$(CO) and HRh(TPPTS)$_2$(CO) the sulfonate groups are farther apart in the former. This is shown in the scale drawings of these two complexes in Fig. 1. The bis phosphine complex of **1** with rhodium should be more stable relative to the bis phosphine complex of TPPTS in solvents of low dielectric constant. Since it is generally accepted that the bis phosphine complex is required for good selectivity to linear aldehydes in hydroformylation catalysis it is not surprising that **1** should show better selectivity than TPPTS in aqueous methanol.

The phosphine BISBI [10] is well known to generate very selective rhodium hydroformylation catalyst. A water soluble version of BISBI has been prepared by direct sulfonation [11]. Also, we previously reported an amphiphilic version of BISBI with three methylene groups, **3** [12]. We have now prepared the analog with ten methylene groups, **2**. As with **1** both better selectivity and activity is observed with the amphiphilic ligand compared to TPPTS although with **2** the activity advantage is not as great. Results are given in Table 2. Turnover frequencies are not reported since the conversions are all relatively high at the longer reaction times. When **1** and **2** are compared directly, better activity is observed with the former and similar selectivity to linear aldehydes is observed for the two ligands.

The ligands **1** and **2** were also investigated in the rhodium catalyzed hydroformylation of tetradecene. As expected, lower conversions are observed for this highly insoluble substrate even in aqueous methanol as the solvent. The reactions were run for 20 h to obtain significant conversion to aldehydes. The results are given in Table 3 and shown graphically in Fig. 2. For comparison, results are also shown for TPPTS, **3**, the monodentate phosphine **4**, as well as **1** and **2**. Ligands **3** and **4** are shown schematically in Fig. 2. The chelating ligand **3** gives the best reaction selectivity although direct comparison is difficult since the activity for this ligand is so poor. The best combination of activity and selectivity is again observed with **1**. The long reaction times resulted in some alcohol formation with **1** only as the modifying ligand.

The concept of using amphiphilic sulfonated phosphines in two- phase catalysis clearly has merit. The ligands show significantly improved rates compared to TPPTS and they retain good reaction selectivity in

Table 3
Two phase hydroformylation of 1-tetradecene

	TPPTS	PC3-TS	BISBI-C3-TS	**1**	**2**
Yield (%); TOF (h^{-1})	8.5; 2.1	12; 3.0	8.3; 2.1	74 [a]; 18.5	49; 12.3
% of 1-pentadecanal	76	80	95	88	71

Reaction Conditions: reaction time, 20 h; reaction temperature, 120°C; initial pressure, 210 psi (at 25°C); stirring rate is 350 rpm; [Rh] =0.0049 M. Note: PC3-TS is a monodentate ligand like **1** but with three methylene groups. Likewise, BISBI-C3-TS, is the analog of **2** with three methylene groups.
[a]Including 11% of pentadecanols.

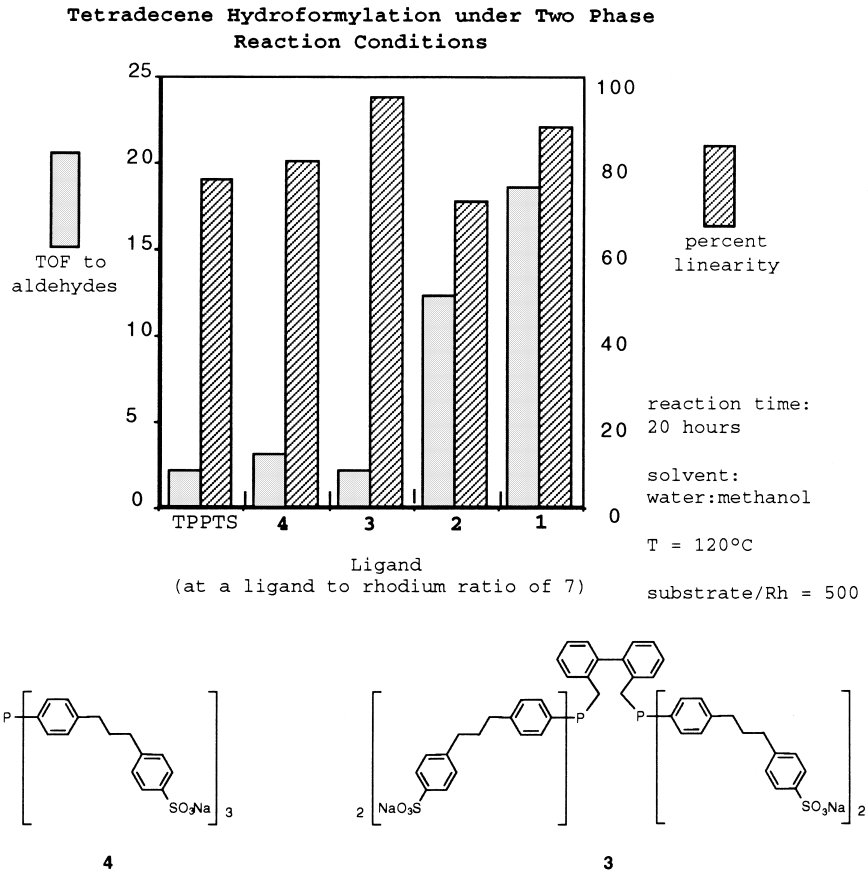

Fig. 2. Bar-graph representation of the activity and selectivity for various sulfonated ligands in the two phase hydroformylation of 1-tetradecene in aqueous methanol.

aqueous alcohol solvents. Importantly, the ligands are highly water soluble yet do not lead to the formation of stable emulsions. This enables the efficient separation of catalyst and products.

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