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New water soluble chelating phosphines for aqueous phase catalysis

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Abstract

The syntheses of two chelating phosphines with pendant groups -*p*-C_6H_4-$(CH_2)_3$-C_6H_5, 2,2′-bis{di[*p*-(3-phenylpropyl)phenyl]phosphino}-1,1′-binaphthalene (BINAP type phosphine) and 2,2′-bis{di[*p*-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1′-biphenyl (BISBI type phosphine), are described. These phosphines are further sulfonated with concentrated H_2SO_4 under mild conditions to yield their tetrasulfonated water soluble analogs. Two phase hydroformylation of octene-1 with in situ rhodium catalyst of the water soluble phosphines is investigated. The results indicate that the rhodium catalyst with sulfonated BISBI type phosphine offers both good activity under two phase conditions, due to the surface activity of the phosphine and excellent selectivity (97% of 1-nonanal, at Rh/P ratio of 1/9).

Keywords: Aqueous phase catalysis; Phosphines; Octene hydroformylation

1. Introduction

The recent progress in the development and application of water soluble catalysts for oxo synthesis and other catalytic reactions has been extensively reviewed [1–3]. There continues to be rapid growth in the scientific [4–17] and patent [18–22] literature on the topic. Current applications of water soluble catalysts are limited to substrates that have significant water solubility. The ability to use water soluble catalysts with poorly water soluble substrates would represent a breakthrough in the practice of hydroformylation of higher olefins [23]. To this end much of the recent work in the field has focused on improving rates and selectivities in the hydroformylation of these olefins over water soluble catalysts. One promising approach is the use of phosphine ligands which improve the solubility of the substrate in the aqueous catalyst containing phase [4–7,23,24]. Phosphines that have the ability to solubilize substrates tend to be mildly surface active and have been shown to aggregate under various conditions [24].

It is well known in the hydroformylation literature that the chelating phosphine, 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl, BISBI, can be used with rhodium to give very

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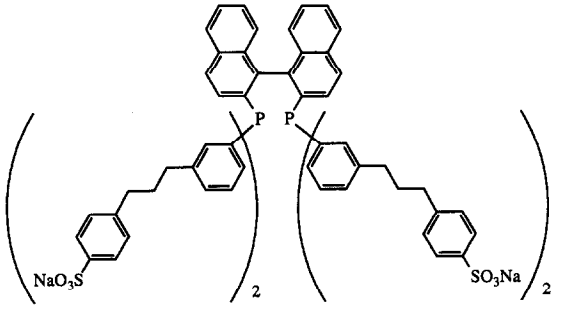
selective catalysts for the hydroformylation of propene [25]. Highly sulfonated versions of BISBI have been prepared for use under two phase reaction conditions and theses have been shown to retain their selectivity for the hydroformylation of propene in water. The selectivity is also good for the hydroformylation of 1-hexene in water although the rates are low with this substrate due to the poor water solubility of the 1-hexene [26].

We have shown previously that the incorporation of surface active groups into phosphines can improve the solubility of substrates in water and that reaction rates improve when these ligands are used to modify transition metal catalysts [24]. Here we show that the group (-C_6H_4)(CH_2)$_3$(C_6H_5) can be included in chelating phosphines that contain the binaphthyl or the 2,2′-dimethyl-1,1′-biphenyl backbone. Furthermore the resulting phosphines are selectively sulfonated to yield highly water soluble phosphines; the new phosphines, **1** and **2**, are shown schematically below. Rhodium catalysts of **2** are more active for the two phase hydroformylation of 1-octene than the corresponding trisulfonated triphenylphosphine, TPPTS, catalysts at low ligand to rhodium ratios, while the binaphthyl phosphine, **1**, shows equivalent or less activity than TPPTS. The BISBI type ligand, **2**, shows similar reaction selectivity to BISBI itself.



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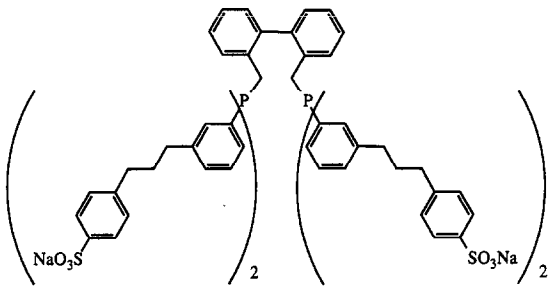

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2. Experimental

All reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. All solvents used in the reactions were dried and deoxygenated by distillation under argon prior to use. Octene-1, nonane, Rh(acac)$(CO)_2$, racemic 1,1′-binaphthalene-2,2′-diol, trifluoromethanesulfonic anhydride, anhydrous DMF, $NiCl_2$(dppe), 1,4-diazabicylo[2,2,2]octane (DABCO) and sulfuric acid were purchased from Aldrich. The CO/H_2 (50/50) was purchased from Airco. Compound **3**, *p*-(3-phenylpropyl)phenylchloride was prepared as described previously [24]. 2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthalene, **4**, was made by a literature method [27].

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 RU 400 NMR spectrometer at 399.052, 100.577 and 161.903 MHz, respectively. The key to the NMR data is: s, singlet; d, doublet; t, triplet; quart, quartet; quin, quintet; m, multiplet; br, broad; asterisk, pseudo. Rhodium and phosphorus analyses were accomplished by inductively coupled plasma analysis (Perkin Elmer ICP-6000) at

213.620 nm and 1.5 kW power. For the phosphorus analysis a sample of independently analyzed TPPTS was used as a secondary standard. Both the standard and samples of the new sulfonated phosphines were dissolved in aqueous methanol (50/50, v/v) for aspiration into the spectrometer.

2.1. The synthesis of di[p-(3-phenylpropyl)phenyl]chlorophosphine, 5

A sample of *p*-(3-phenylpropyl)phenyllithium (8.1 g, 40 mmol) in 150 ml solvent (Et_2O/THF 1/1), which was prepared as previously described, was added dropwise to CH_3OPCl_2 (2.66 g, 20 mmol) in 70 ml solvent (Et_2O/THF 1/1) at −70°C. The addition was completed in 2 h. The reaction mixture was stirred overnight at room temperature and then brought to reflux for 2 h. The precipitate was filtered and the solvent of the solution was removed by applying vacuum. PCl_3 (15 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 the byproduct. The product, di[*p*-(3-phenylpropyl)phenyl]chlorophosphine, was obtained as a pale yellow viscous oil with a 90% yield. ^{31}P NMR (δ in $CDCl_3$) 83.6 (s).

2.2. The synthesis of di[p-(3-phenylpropyl)phenyl]phosphine, 6

A sample of di[*p*-(3-phenylpropyl)phenyl]chlorophosphine (6.0 g, 13.1 mmol) was dissolved in 150 ml THF and Li (0.185 g, 26.2 mmol) was chopped directly into the reaction flask under Ar. A deep red solution resulted and all the lithium was consumed in 4 h. The solvent was removed by vacuum and 100 ml diethyl ether was added. The organic phase was washed with H_2O three times, 20 ml each, separated and dried over $MgSO_4$. Ether was then removed by vacuum and the final product was obtained as a pale yellow oil in quantitative yield. $^{31}P\{^1H\}$ NMR (δ in $CDCl_3$) −42.5 (s), ^{31}P NMR (δ in $CDCl_3$) −42.5, d, $^1J_{H\text{-}P} = 211$ Hz.

2.3. The synthesis of 2,2′-bis{di[p-(3-phenylpropyl)phenyl]phosphino}-1,1′binaphthalene, 7

The synthesis was carried out by a modification of a literature method for the synthesis of 2,2′-bisdiphenylphosphino-1,1′-binaphthyl [28]. The reaction of 2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthalene, **4**, with di[*p*-(3-phenylpropyl)phenyl]phosphine, **6**, yields 2,2′-bis{di[*p*-(3-phenylpropyl)phenyl] phosphino}-1,1′-binaphthalene, **7**.

Compound **6** (0.48 g, 1.15 mmol) was added to a solution of $NiCl_2$(dppe) (0.106 g, 0.2 mmol) in 5 ml DMF at room temperature. The resulting mixture was placed in an oil bath which had been preheated to 100°C. 30 min later a solution of **4** (1.1 g, 2.0 mmol) and DABCO (0.9 g, 8.0 mmol) in 6 ml DMF was added at once. The color of the solution changed immediately to dark brown. Three additional portions of **6** (0.5 g each) were added to the reaction mixture at 1, 3 and 7 h. The solution was kept at 100°C for 4 days. Most of the DMF was removed by vacuum distillation and 40 ml diethyl ether was added to dissolve organic product. After being washed twice with 20 ml H_2O each, ether was removed to yield a brown viscous oil. The final product, **7**, was separated as a yellow waxy solid from the oil by silica gel column using hexane/diethylether (10/1). The overall yield of the reaction is 45%. ^1H NMR (δ in $CDCl_3$): 1.87 (m, 8H); 2.53 (m, 8H); 2.59 (m, 8H); 6.7–7.9 (m, 48H). ^{13}C NMR (δ in $CDCl_3$): 32.73 (s, 4C); 35.13 (s, 4C); 35.41 (d, $^5J_{c-p}$ = 10.1 Hz, 4C); 125.58 (s, 2C); 125.71 (s, 4C); 126.24 (s, 2C), 127.51 (s, 2C); 127.91 (s, 2C); 128.16 (s, 4C); 128.26 (s, 8C); 128.41 (s, 8C); 132.92 (*t, 8C); 133.30 (s, 2C); 134.26 (*t, 8C); 135.10 (d, $^1J_{c-p}$ = 15.1 Hz, 4C); 136.12 (d, $^1J_{c-p}$ = 10.2 Hz, 2C); 141.61 (s, 2C); 142.24 (d, $^4J_{c-p}$ = 3.8 Hz, 4C); 142.50 (s, 4C). ^{31}P NMR (δ in $CDCl_3$): −16.3 (s). Mass spectroscopy

(FAB in a glycerol matrix yielded the phosphine oxide): 1055 ($M^+ + 1$).

2.4. Synthesis of 2,2'-bis{di[p-(3-p-sulfonatophenylpropyl)phenyl]phosphino}-1,1'-binaphthalene, 1

Compound **7** (1.0 g, 0.9 mmol) was chilled to −78°C and 8 ml H_2SO_4 (96.1%) was added. The mixture was then allowed to warm up and to be stirred at room temperature. 10 h later the mixture was neutralized with aqueous NaOH (20%, w/w). The final pH was 8.5. 320 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 20 ml. 200 ml of acetone was then added to generate a white precipitate. The precipitate, **1**, was collected by filtration and dried under vacuum (1.3 g, 95% yield). ^{1}H NMR (δ in CD_3OD): 1.86 (m, 8H); 2.53 (m, 8H); 2.61 (m, 8H); 6.6–7.9 (m, 44H). ^{13}C NMR (δ in CD_3OD): 33.87 (s, 4C); 36.09 (br.s, 8C); 126.28 (s, 2C); 127.13 (s, 8C); 128.38 (s, 2C), 128.75 (s, 2C); 128.88 (s, 2C); 129.32 (br.s, 12C); 134.25 (*t, 8C); 135.44 (*t, 8C); 136.50 (s, 2C); 137.25 (s, 2C); 142.20 (s, 2C); 143.26 (s, 4C); 144.04 (s, 4C); 146.11 (s, 4C). ^{31}P NMR (δ in CD_3OD): −15.2 (s). Mass spectroscopy (FAB, in glycerol matrix yielded the phosphine): 1525 ($M + Na^+$). Phosphorus analysis calc. 4.12%: found, 3.89%.

2.5. The synthesis of 2,2'-bis{di[p-(3-phenylpropyl)phenyl]phosphinomethyl}-1,1'-biphenyl, 8

The synthesis is a modification of the method for 2,4-bis{di[*p*-(3-phenylpropyl)phenyl]phosphino}pentane [29]. A sample of di[*p*-(3-phenylpropyl)phenyl]chlorophosphine (6.0 g, 13.1 mmol) was dissolved in 150 ml THF and Li (0.185 g, 26.2 mmol) was chopped directly into the reaction flask under Ar. A deep red solution resulted within 10 min and all the lithium was consumed within 4 h. The solution was then filtered and 2,2'-dibromomethyl-1,1'-biphenyl (2.23 g, 6.5 mmol) in 20 mL THF was added dropwise with an ice-water bath. The color of the solution was slowly changed to pale yellow. The mixture was stirred for an additional 10 h before the solvent was removed by vacuum. 50 ml diethyl ether was added and was washed three times with 20 ml H_2O each. The ether phase was separated and dried over $MgSO_4$. The solvent was then removed by vacuum. The resulting pale yellow viscous oil was purified over silica gel column. 2.3 g (69% yield) of **8** was eluted with Et_2O/hexane (1/10). ^{1}H NMR (δ in $CDCl_3$): 1.83 (m, 8H); 2.51 (m, 16H); 3.06 (*quart, 4H); 6.9–7.2 (m, 44H). ^{13}C NMR (δ in $CDCl_3$): 32.72 (d, $^7J_{c-p} = 3.7$ Hz, 4C); 33.65 (d, $^1J_{c-p} = 16.1$ Hz, 2C); 35.12 (d, $^6J_{c-p} = 2.3$ Hz, 4C); 35.31 (d, $^5J_{c-p} = 13.0$ Hz, 4C); 125.71 (s, 4C); 128.26 (s, 4C); 128.33 (s, 8C), 128.36 (s, 8C); 129.65 (s, 2C); 129.75 (s, 2C); 132.64 (d, $^3J_{c-p} = 18.3$ Hz, 8C); 133.25 (d, $^2J_{c-p} = 19.1$ Hz, 8C); 135.18 (d, $^1J_{c-p} = 14.5$ Hz, 4C); 135.88 (d, $^3J_{c-p} = 9.2$ Hz, 2C); 140.82 (d, $^2J_{c-p} = 4.5$ Hz, 2C); 142.09 (s, 4C); 142.44 (s, 4C). ^{31}P NMR (δ in $CDCl_3$): −11.8 (s). Mass spectroscopy (FAB, from a glycerol matrix yielded only the phosphine oxide): 1055 ($M^+ + 1$).

2.6. Synthesis of tetrasulfonated 2,2'-bis{di[p-(3-phenylpropyl)phenylphosphino-methyl}-1,1'-biphenyl, 2

A sample of 2,2'-bis{di[*p*-(3-phenylpropyl)-phenyl]phosphinomethyl}-1,1'-biphenyl, **8** (2.2 g, 2.2 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 8.5. 320 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 20 ml. 200 ml of acetone was then added to generate a white precipitate. The precipitate, tetrasulfonated 2,2′-bis{di[*p*-(3-phenylpropyl)phenyl] phosphinomethyl}-1,1′-biphenyl, **2**, was collected by filtration and dried under vacuum (2.8 g, 93% yield). ^{1}H NMR (δ in CD_3OD): 1.91 (m, 8H); 2.57 (m, 8H); 2.63 (m, 8H); 3.10 (*quart, 4H); 6.8–7.8 (m, 40H). ^{13}C NMR (δ in CD_3OD): 34.12 (d, $^{1}J_{c-p} = 13.1$ Hz, 2C); 34.15 (s, 4C); 36.13 (s, 4C); 36.20 (s, 4C); 127.08 (s, 8C); 129.36 (s, 8C), 129.77 (s, 4C); 130.70 (s, 2C); 130.75 (s, 2C); 133.75 (d, $^{3}J_{c-p} = 18.3$ Hz, 8C); 134.51 (d, $^{2}J_{c-p} = 19.8$ Hz, 8C); 143.92 (s, 4C); 146.15 (s, 4C). ^{31}P NMR (δ in CD_3OD): −10.7 (s). Mass spectroscopy (FAB, in glycerol matrix yielded the phosphine): 1453 ($M + Na^+$). Phosphorus analysis calc. 4.33%, found 4.12%.

2.7. Catalysis

Two phase hydroformylation reactions of 1-octene with rhodium complexes of **1** and **2** were carried out in a 30 ml capacity stainless steel reaction vessel. The catalysts were 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 ligand. Water was added to adjust the total aqueous methanol volume to 1.56 ml. The substrate, 0.60 ml of 1-octene, 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 the organic phase was 1.0 ml. 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 after cooling 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 35°C (4 min) to 220°C (1 min), at a heating rate of 10°C/min. A special injection port sleeve was installed to facilitate the separation of analytes.

3. Results

3.1. Synthesis

Synthetic routes to phosphines that contain the $-(C_6H_4)(CH_2)_3(C_6H_5)$ group are outlined in this paper. Most of the reactions are well known in phosphine chemistry [30]. The reaction from **6** to **7** is an application of the synthesis described by Cai et al. for the preparation of BINAP [28].

As previously observed during the sulfonation of $P\{(C_6H_4)(CH_2)_3(C_6H_5)\}_3$ and bis-2,4-bis-{di[*p*-(3-phenylpropyl)phenyl] phosphino} pentane, the pendant group, $(C_6H_4)(CH_2)_3(C_6H_5)$, is easily sulfonated at mild reaction conditions in **1** and **2**. The degree of sulfonation is deduced from the mass spectroscopy results combined with NMR analysis. From previous NMR work on sulfonated phosphines, we observe that in the ^{13}C NMR spectrum the carbon that bears the sulfonate group always has a chemical shift downfield from 145 ppm [24,29,31]. In this region of the spectrum for **1** and **2** only one signal is observed consistent with a single site for sulfonation. Of the possibilities, ortho, meta or para sulfonation, para is most likely. Mono substituted alkyl benzenes are ortho–para directing for electrophilic substitution of aromatic rings. It is very unlikely that substitution goes exclusively to the more hindered ortho position. Furthermore in the

monodentate phosphines of the type $P(C_6H_4(CH_2)_nC_6H_4SO_3Na)_3$ only para sulfonation is expected to give the relatively simple proton and carbon NMR spectra that are observed. In **1** and **2** the aromatic region of the spectrum is complicated by the presence of biphenyl and binaphthyl respectively. The mass spectrum indicates that a maximum of four sulfonate groups have been incorporated per phosphine.

Direct sulfonation of BISBI and BINAP require high concentrations of SO_3 in H_2SO_4 and long reaction times. The more vigorous reaction conditions leads to some oxidation of the phosphorus to yield phosphine oxides. In addition to sulfonation of the $P(C_6H_5)_2$ groups some sulfonation occurs on the aromatic biphenyl or binapthyl group [26,32].

The unsulfonated phosphines **7** and **8** are more susceptible to oxidation than the sulfonated phosphines, **1** and **2**, as evidenced by the fact that in the FAB mass spectrum under otherwise identical conditions the former yield only the phosphine oxide in the mass spectrum while **1** and **2** do not oxidize.

3.2. Two phase hydroformylation of 1-octene with 1 and 2

Hydroformylation results of 1-octene with **1** and **2** are summarized in Table 1. For comparison, results from the two phase hydroformylation of 1-octene with TPPTS under the same reaction conditions are also listed. Ligand to rhodium ratios up to 7:1 for **1** and 14:1 for **2** were investigated. Higher ratios, of interest commercially, were not studied due to limited quantities of ligand. It is noted that in the case of **2** activity begins to drop at ratios of 14:1. The catalyst-containing phase consists of 50% H_2O and 50% methanol. The presence of methanol is due to the preparation of in situ catalyst. Leakage of methanol into the organic phase after the reaction is less than 0.5%. Previously we have shown that rhodium/TPPTS in methanol show higher activity but suffer poorer selectivity than rhodium/TPPTS in water alone as the solvent [24,33]. More recent work by Fell suggests that addition of methanol as a cosolvent is a general way to improve activity in two phase hydroformylation catalyst systems [5]. The concentration of rhodium in both the organic and aqueous phases after catalysis was checked by ICP analysis of the different phases. These results along with a more detailed analysis of the reaction products are summarized in Table 2. The detection limit for rhodium analysis with the ICP is $\sim 1/3$ ppm. Rhodium is not detected in the organic phase by ICP after the reaction. Due to dilution of the small sample to facilitate aspiration into the ICP apparatus, an upper limit on the concentration of rhodium in the organic phase is set at 3 ppm. The organic phase is colorless in all reactions suggesting that the sulfonated phosphines, like TPPTS, are very efficient at keeping rhodium in the aqueous

Table 1
Two phase hydroformylation of 1-octene with **1**, **2** and TPPTS

Rh/P ratio	1		2		TPPTS	
	yield (%)	n/b (%/%)	yield (%)	n/b (%/%)	yield (%)	n/b (%/%)
1:2	29	74/26	45	68/32	30	68/32
1:3	31	74/26	57	76/24	37	70/30
1:5	14	75/25	69	88/12	52	75/25
1:7	5.3	70/30	73	94/6	54	76/24
1:9	—	—	67	97/3	69	76/24
1:14	—	—	30	98/2	—	—

Reaction conditions: reaction time, 5 h; reaction temperature, 120°C; initial pressure, 210 psi (at 25°C); stirring rate is 350 rpm; $[Rh] = 4.9 \times 10^{-3}$ M.

Table 2
Results from two phase hydroformylation of octene-1 at Rh/phosphorus = 1/7

	TPPTS	2
Yield of C_9 aldehydes (%)	58	74
Selectivity (% of 1-nonanal)	74	93
C_8 hydrocarbons (%)	34 (5)	23 (14)
C_9 alcohols (%)	7.1	2.5
Heavyends (%)	0.8	0.2
[Rh] in organic phase (ppm)	not detected	not detected
[Rh] in aqueous phase (ppm)	508	514

Reaction conditions: [Rh] = 502 ppm, Rh/octene-1 = 1/500, temperature = 120°C, pressure = 210 psi at room temperature, Reaction time = 5 h, stirring rate = 350 rpm. The [Rh] is determined by the ICP method. Both standard and samples are prepared in MeOH.

alcoholic phase. The mass balance for rhodium as indicated by analysis of the catalyst-containing phase is good.

The tetrasulfonated BISBI ligand, **2**, is the best ligand of these phosphines. At a ligand/Rh ratio of 7–9, the rhodium catalyst with **2** offers good reactivity and selectivity towards 1-nonanal. Detailed product distribution is given in Table 2. Increased activity, compared to the Rh/TPPTS system, may be explained in part by the surface activity of the ligand. At high ligand to rhodium ratios the TPPTS ligand shows similar activity. In agreement with previous results the selectivity of TPPTS catalysts suffers in aqueous methanol as the reaction solvent. Excellent selectivity is observed with **2**. It was previously observed that the trisulfonated monodentate ligand, $P\{(C_6H_4)(CH_2)_3(C_6H_4SO_3Na)\}_3$, **9**, also yields rhodium catalysts of good selectivity in aqueous methanol. This was attributed to reduced electrostatic repulsions in **9** which is much larger than TPPTS. In the case of **2** the reaction selectivity is similar to its unsulfonated BISBI analog and may be attributed to the special steric effect of the nine membered chelating ring. On the other hand, the rhodium catalyst with **1** as the modifying ligand forms a seven membered chelate. Both the poor activity and selectivity may be attributed to the chelate ring by analogy to other simple chelating phosphines in the hydroformylation reaction [34].

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