

Two-Phase Hydroformylation of Octene-1 with Rhodium Complexes of $P[C_6H_4(CH_2)_mC_6H_4-p-SO_3Na]_3$ ($m = 3, 6$). Rate and Selectivity Enhancement with Surface-Active Phosphines

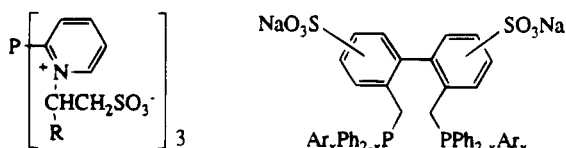
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Summary: The new sulfonated phosphines $P[C_6H_4(CH_2)_mC_6H_4-p-SO_3Na]_3$ ($m = 3, 6$) are synthesized by direct sulfonation of $P[C_6H_4(CH_2)_mC_6H_5]_3$ with concentrated sulfuric acid. Dynamic light scattering experiments show that the sulfonated phosphines aggregate in 0.25 M NaCl solution. These aggregates have a hydrodynamic radius of 20 and 32 Å, respectively, for the phosphines with $m = 3$ and $m = 6$. In the two-phase hydroformylation of octene-1 the rhodium catalysts derived from the new phosphines show significant improvement over catalysts generated from trisulfonated triphenylphosphine. Not only are the initial rates faster but also the reaction selectivity as reflected by the n/b ratio is better; specifically, at a ligand/rhodium ratio of 10 the n/b values are 8.0 and 9.5, respectively, for $m = 3$ and $m = 6$ compared to 3.6 for trisulfonated triphenylphosphine.

The surface-active character of sulfonated phosphines was noted by Wilkinson et al. in their investigation of the sodium salt of monosulfonated triphenylphosphine (TPPMS) as a water-soluble ligand for the two-phase hydroformylation of hexene-1.¹ Separately it has been shown that the addition of surfactants to hydroformylation catalysts derived from trisulfonated triphenylphosphine (TPPTS) increases the rate of reaction for the two-phase hydroformylation of hexene-1.² Recently a class of ligands specifically designed to be surface active, **1**,



$R = C_nH_{2n+1}$, $n = 6, 12$

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$Ar_xPh_{2-x}P$

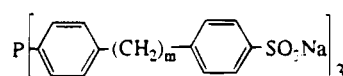
$Ar = m-C_6H_4SO_3Na$

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has been reported; these show improved rates for the hydroformylation of liquid olefins in water.³ On the other hand, the relative rate of hexene-1 hydroformylation, compared to propylene, with water-soluble rhod-

ium catalysts derived from sulfonated BISBI, **2**, is low,⁴ and the same effect is observed for catalysts derived from TPPTS.⁵ This can be attributed to the poor solubility of hexene in water.

Here we describe two new phosphines, **3a** and **3b**, that may have some surface activity. These show not



$m = 3, 6$

3a and 3b

only improved reaction rates in aqueous methanol but also improved selectivity for linear aldehydes in the hydroformylation of octene-1 compared to catalysts derived from TPPTS. Furthermore, it is shown by light-scattering experiments that the phosphines **3a** and **3b** aggregate in aqueous NaCl solution. Formation of small aggregates may be responsible for improved reaction rates at high ligand concentrations.

The phosphines **3a** and **3b**⁶ are synthesized by sulfonation of the phosphine generated from the reaction of $C_6H_5(CH_2)_mC_6H_4Li$ with PCl_3 . The sulfonation procedure follows the method previously described by us.⁷ The sulfonated phosphine **3a** is soluble in water to the extent of 200 mg/mL; neither **3a** nor **3b** is soluble in simple hydrocarbons, including the nonanals produced during hydroformylation.

Catalytic results for the hydroformylation of octene-1 are summarized in Figures 1 and 2 at phosphine/

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(5) (a) Kuntz, E. *French Patent* 2,314,910, 1975. (b) Kuntz, E. *German Patent* 2,627,354, 1976. (c) Kuntz, E. *U.S. Patent*, 4,248,802, 1981.

(6) **3a** was recrystallized from aqueous methanol. Analytical data: ³¹P NMR (D_2O) -8.41 ppm (s); ¹³C NMR (D_2O) 31.68 (s), 34.42 (s), 34.55 (s), 125.38 (s), 128.43 (s), 128.91 (d, $J_{PC} = 4.5$ Hz), 133.60 (d, $J_{PC} = 19.0$ Hz), 140.12 (s), 143.97 (s), 145.50 ppm (s); ¹H NMR (D_2O) 1.32 (br s, 6H), 2.11 (br s, 12H), 6.65 (br s, 6H), 6.73 (br s, 6H), 7.02 (br s, 6H), 7.50 ppm (br s, 6H). Anal. Calcd for $C_{45}H_{42}Na_3O_9PS_3 \cdot 3H_2O$: C, 55.33; H, 4.92. Found: C, 55.19; H, 4.88. **3b** was recrystallized from aqueous methanol. Analytical data: ³¹P NMR (D_2O) -7.96 ppm (s); ¹³C NMR (D_2O) 28.89 (s), 29.19 (s), 30.70 (s), 30.92 (s), 35.27 (s), 125.51 (s), 128.24 (s), 128.50 (br s), 133.58 (d, $J_{PC} = 19.4$ Hz), 140.40 (s), 143.04 (s), 145.61 (s), 133.16 ppm (d, $J_{PC} = 8.0$ Hz); ¹H NMR (D_2O) 1.00 (br s, 12H), 1.19 (br s, 6H), 1.27 (br s, 6H), 2.20, 2.26 (br s, 6H), 6.81 (br s, 6H), 6.86 (br s, 6H), 7.10 (br s, 6H), 7.60 ppm (br s, 6H). Catalytic reactions were done with a sample that contained 5% by weight Na_2SO_4 . Three fractional crystallizations were required to give an analytically pure sample. Anal. Calcd for $C_{45}H_{42}Na_3O_9PS_3 \cdot 3H_2O$: C, 58.80; H, 5.99. Found: C, 58.25; H, 5.73.

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(2) Bahrmann, H.; Cornils, B.; Konkol, W.; Lipps, W. *German Patent* 3,412,335, 1985.

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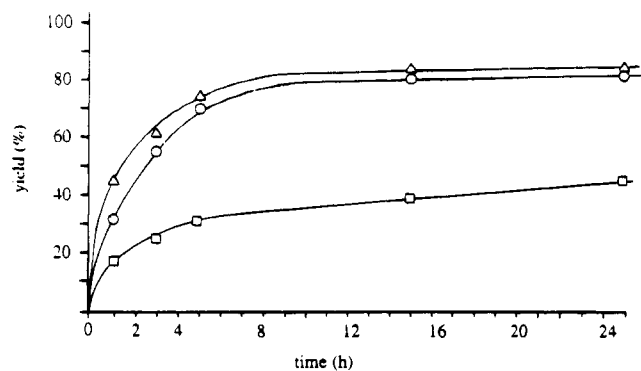


Figure 1. Reaction yield as a function of time for the ligands TPPTS (□), **3a** (Δ), and **3b** (○) in the rhodium-catalyzed hydroformylation of octene-1 at a L/Rh(acac)-(CO)₂ ratio of 2.

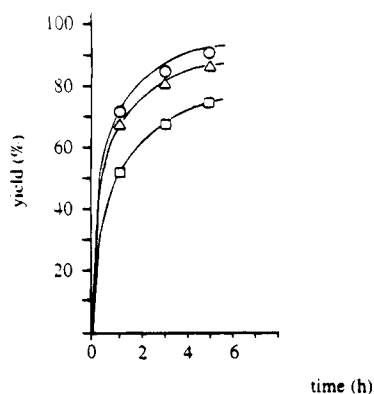


Figure 2. Reaction yield as a function of time for the ligands TPPTS (□), **3a** (Δ), and **3b** (○) in the rhodium-catalyzed hydroformylation of octene-1 at a L/Rh(acac)-(CO)₂ ratio of 10.

rhodium ratios of 2 and 10, respectively.⁸ Significant activity for alcohol formation is seen at high conversion for all the catalysts;⁹ the reaction yield refers to total products of aldehyde plus alcohols. The yield of nonanols represents up to 10% of the total products at conversions greater than 80%. To indicate the relative initial rate of reaction, the average turnover frequencies, in the first 1 h of reaction, are presented in Table 1. Reaction selectivities, as normal to branched product ratios, are given in Table 2 ((total linear products)/(total branched products including alcohols)).

For a given ligand the turnover frequency in the first 1 h of reaction is faster at L/Rh = 10 than at L/Rh = 2.

(8) The catalyst solutions were prepared from a methanol solution of Rh(acac)(CO)₂ and a ligand solution in deionized water. The rhodium concentration was 0.005 M in the aqueous methanol (1/1) layer, and the phosphine concentration was either 0.01 or 0.05 M. Octene-1 and nonane were added as the substrate phase. The initial pressure was 19.5 atm at 25 °C, and the octene-1/Rh ratio was 500/1 in all reactions. After the reaction vessel was loaded and pressurized with CO/H₂, the reaction was initiated by placing the reaction vessel into a temperature bath preheated to 120 °C. The reactor volume was 30 mL. Analysis of the products was accomplished on a Varian 330 GC equipped with an HP-1 (25 m × 0.32 mm × 0.52 μm) column. The temperature program was 50 °C (2 min) to 220 °C (2 min) at a rate of 10 °C/min; the retention times were 8.2 min for linear nonanal and 6.8–7.5 min for the branched isomers of nonanal. The product nonanals have no appreciable solubility in aqueous methanol; no aldehydes are detected by NMR or GC analysis of the aqueous layer. In all catalytic reactions the organic phase was colorless; in a recycling test the organic phase recovered from a catalytic run showed no activity for the hydroformylation of 1-heptene.

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Table 1. Average Turnover Frequency^a in the First 1 h of Reaction^b

	L/Rh = 2	L/Rh = 10
TPPTS	90	260
3a	225	335
3b	160	360

^a mol of aldehyde (mol of Rh)⁻¹ h⁻¹. ^b Conditions: reaction temperature, 120 °C; initial pressure, 19.5 atm; [Rh] = 0.0005 M; stirring rate, 260 rpm.

Table 2. Reaction Selectivity at Highest Conversion^a

	L/Rh = 2		L/Rh = 10	
	yield (%)	n/b	yield (%)	n/b
TPPTS	47	2.4	78	3.6
3a	88	3.0	85	8.0
3b	84	3.3	88	9.5

^a Conditions: reaction temperature, 120 °C; initial pressure, 19.5 atm; [Rh] = 0.0005 M; stirring rate, 260 rpm.

This is true for TPPTS as well as for the new ligands **3a** and **3b**. The fact that the rates improve at higher ligand ratios is in contrast to the case for Rh/PPh₃ catalysts, in which reaction rate drops at high ligand concentrations.⁹ It has been suggested that catalysis under two-phase reaction conditions with water-insoluble olefins is mass transfer limited.¹⁰ Thus, it appears that the water-soluble phosphines not only serve to complex the rhodium but also facilitate the mixing of the immiscible phases. The latter effect apparently is more significant in determining the reaction rate. (It should be noted that the catalytic solutions in the present study contain methanol, which should increase the solubility of octene-1 in the aqueous phase.)

At a constant L/Rh ratio the rates improve on going from TPPTS to **3a** and **3b**. This may be explained by better mixing of the phases, since the phosphines **3a** and **3b** may be more surface active than TPPTS. A dramatic increase in rate is also observed on going from TPPTS at L/Rh = 2 to TPPTS at L/Rh = 10. The improvement in rate with an increase in TPPTS concentration is more difficult to explain (vide infra).

Dynamic light-scattering experiments were done in an attempt to elucidate the mechanism for increased reaction rate.^{11,12} These were done at ambient temperature (22 °C) and atmospheric pressure on aqueous solutions of the free phosphines. For the ligand **3a** at 0.05 M concentration the average hydrodynamic radius was consistently measured to be 7 Å. This demonstrates that no aggregation of the ligand occurs under these conditions. At a NaCl concentration of 0.25 M the average hydrodynamic radius increases to 20 Å. The corresponding value for a sample of **3b** that contained 5% by weight Na₂SO₄ is 20 Å. In 0.25 M aqueous NaCl the hydrodynamic radius increases to 32 Å. The salt solutions of **3a** and **3b** foamed when shaken, characteristic of micelle formation. Light-scattering experiments on aqueous solutions of TPPTS showed no evidence for aggregation at all concentrations of TPPTS and NaCl investigated.

The hydrodynamic radius of 7 Å for **3a** in water is consistent with isolated molecules of the ligand. The

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(12) The light-scattering experiments were done on a Biotage dp-801 molecular size detector. The solutions were prepared in degassed, distilled, deionized water and filtered twice through a 0.1 μm syringe filter.

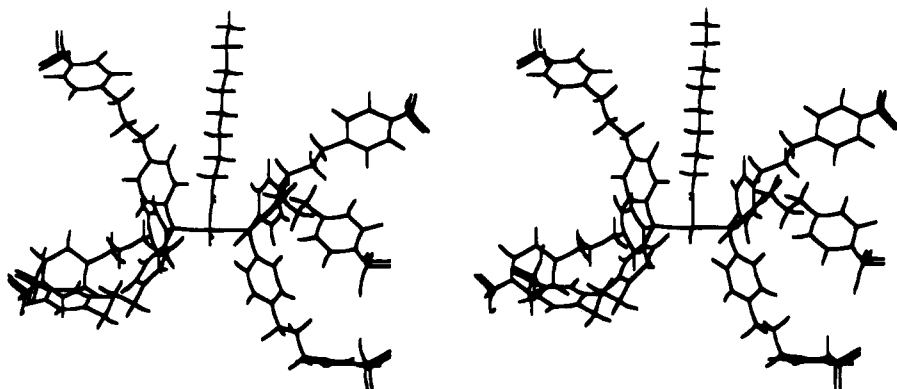


Figure 3. Stereoview of a scale drawing of the possible reaction intermediate $\text{trans-Rh}^{\text{I}}(\mathbf{3a})_2[\text{CO}(\text{CH}_2)_7\text{CH}_3]$. The drawing was generated by the program ALCHEMY and does not represent a fully minimized structure. The phenyl rings bonded to phosphorus are twisted to give a propeller motif, and the methylene groups are arranged to give maximum extension of the phenyl sulfonate groups. A trans arrangement at the rhodium is shown.

phosphine is comprised of three linear pendant groups terminated with a sulfonate group and linked at the hydrocarbon end by phosphorus. In the absence of added salt, electrostatic repulsions between the sulfonate groups are expected to define the solution conformation. This generates a trigonal-planar arrangement of sulfonate groups with respect to the phosphorus atom. Aggregation apparently can take place as the ionic strength of the solution is increased by the addition of salt. If the relationship of the sulfonate groups to the phosphorus atom is pyramidal, then a tetrahedral array of four phosphines, with the phosphorus atoms comprising the hydrophobic core of a small micelle, fits the experimental hydrodynamic radius of 20 Å.

Although light-scattering experiments show that the sulfonated ligands can aggregate in aqueous salt solution, the situation under two-phase catalytic reaction conditions must be more complicated. For example, in no case is a stable emulsion formed when all the reaction components are present, i.e. (acac)Rh(CO)₂, sulfonated phosphine, water, methanol, octene-1, and nonane. No salts are added to the reaction mixture, and the solutions do not foam when shaken. After the catalytic reactions are complete, the water and hydrocarbon phases rapidly separate. However, light-scattering experiments on aqueous solutions generated from (acac)Rh(CO)₂ and **3b** at a L/Rh ratio of 2 showed the presence of aggregates with a hydrodynamic radius of 19 Å.

Another qualitative test for the formation of micelles is the extent of dissolution of a poorly water soluble dye, for example Orange OT.¹³ The dye dissolves more rapidly and dissolves to a greater extent in solutions that contain micelles. Aqueous solutions of **3a**, without salt, dissolve Orange OT in a manner consistent with micelle formation.

At L/Rh ratios of 10 the *n/b* ratios are 3.8, 8, and 9.5 for TPPTS, **3a**, and **3b**, respectively, at 78–88% conversion. A ligand excess of 10/1 is relatively modest for the observation of *n/b* ratios as high as 8. The reaction selectivity may be due to special steric constraints in water provided by the sulfonated phosphines **3a** and **3b**. We speculate that rhodium complexes of the two new phosphines can mimic a small micelle with six pendant sulfonate groups and that the region near the rhodium

provides a hydrophobic pocket for binding the olefin substrates. This is shown schematically in Figure 3. The arrangement is consistent with the measured hydrodynamic radius of 19 Å for rhodium solutions of **3b**. The proportion of rhodium bearing two phosphines under catalytic conditions is likely to increase as the P/Rh ratio is increased.

The improved reaction rate for octene-1 hydroformylation at high concentrations of TPPTS (Figure 2) is surprising. Since TPPTS does not aggregate in water (vide supra), a different mechanism for rate enhancement must be operative.

In the example of ligand **1** it was argued that micelles may be formed under reaction conditions.³ The activity of rhodium hydroformylation catalysts reported with **1**³ under conditions similar to those in the present study are comparable to the best results obtained with **3b**. (Direct comparisons are difficult to make due to different concentrations of reagents and different conditions for mixing in the two-phase reactions.) However, catalytic reactions with **1** under two-phase reaction conditions show poorer reaction selectivity (*n/b* = 2.5–4)³ compared to tris(2-pyridyl)phosphine (*n/b* = 13)¹⁴ for the hydroformylation of terminal olefins.

The data presented here show that it is possible to modify reaction rate and selectivity with water-soluble ligands that have the potential to aggregate in aqueous solution. The degree of surface activity in the ligands $\text{P}[\text{C}_6\text{H}_4(\text{CH}_2)_m\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3$ can be modified simply by changing the number of methylene groups in the phosphines.

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