

# Synthesis and catalytic chemistry of two new water-soluble chelating phosphines

## Comparison of ionic and nonionic functionalities

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### Abstract

Two new water-soluble chelating alkyl phosphines are described. The compounds are prepared by radical addition of allylic substrates to 1,2-bis(phosphino)ethane in methanol. Complexes with the stoichiometry of 1.5:1 diphosphine:rhodium(I) are effective in the hydrogenation of the olefins 1-hexene and crotonaldehyde. Catalyst solutions prepared with the ligand DSPrPE were found to be 3 times more active than those prepared with TPPTS (triphenylphosphine trisulfonate) under identical conditions. Several rhodium complexes of the two ligands are described, and the crystal structure of Rh{1,2-bis[(di-hydroxypropyl)phosphino]ethane}<sub>2</sub>Cl was determined.

**Keywords:** Phosphine; Rhodium; Water-soluble; Biphasic; Hydrogenation; Crystal structure

### 1. Introduction

Biphasic organometallic catalysis has received considerable attention over the last 18 years [1]. Systems in which the catalyst and substrates/products are immiscible, such as the well-publicized Rhône–Poulenc hydroformylation process, are advantageous because the catalyst and products are easily separated [2]. Because of the interest in biphasic systems, a large number of new water-soluble phosphorus ligands have been prepared as a way to impart water-solubility to metal complexes [3]. The

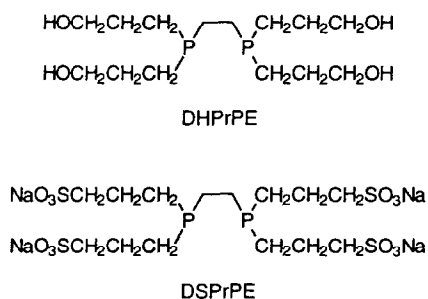
sulfonated triphenyl phosphines were the first commercially successful and widely published water-soluble phosphine ligands [4]. Not surprisingly, these ligands have become the template for further ligand development, and the majority of ligands synthesized to date are sulfonated phenyl phosphine derivatives [5]. Their widespread use is in part due to their relative ease of preparation and their high water-solubility [6].

Because of the attention given to sulfonated phenyl phosphines, relatively few water-soluble alkyl phosphorus ligands have been developed. Several hydroxy-alkyl phosphines have been prepared, but the catalytic activity of rhodium complexes with these ligands was either low or

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not investigated [7,8]<sup>1</sup>. Other nonphenyl containing phosphines include those with alcoholic and polyalkyl ether pendant groups [10]<sup>2</sup>, PTA [11], carboxylated phosphines [12], and a series of alkyl phosphines with sulfonated phenyl end-groups [13]. In addition, there are several examples of mono- and di-phenyl phosphines with one or two functionalized alkyl groups that are attached to the phosphorus and which are water soluble [14].

In response to the paucity of water-soluble phosphines that do not contain phenyl groups, we have developed a pair of new, chelating alkyl phosphines that are water-soluble by virtue of having hydroxyl and sulfonate end-groups.



With this pair of ligands, we were able to compare the effect on catalytic reactions of altering the water-solubilizing functionality from ionic to nonionic. Furthermore, it is of interest to note that salt effects have been implicated in the kinetics of catalytic hydrogenation reactions with ruthenium phosphine complexes [15]. Salt effects also led to changes in the kinetics and product distributions in hydroformylation reactions with rhodium phosphine complexes [16]. We now have a ligand system in which these salt effects can be studied without the large changes in the ionic strength that are inherent to solutions of TPPTS (triphenylphosphine trisulfonate). In this paper, we describe the synthesis and characterization of the new chelating ligands, their complexes with rhodium, and a com-

parison of their catalytic activity in the biphasic hydrogenation of olefins.

## 2. Experimental

All manipulations of air sensitive materials were carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmospheres glove box.

### 2.1. Reagents and instrumentation

Allyl sulfonic acid sodium salt (TCI America, Portland, OR), allyl alcohol (Aldrich), 1,2-bis(phosphino)ethane (Strem), and VAZO 67 (2,2'-azobis(*iso*-butyronitrile); DuPont) were all used as received. 1-Hexene (Sigma) was dried over sodium and distilled under N<sub>2</sub>. Anhydrous rhodium trichloride (Engelhard) was dried under vacuum for 3 h prior to use. The catalyst precursor [Rh(COD)Cl]<sub>2</sub> was prepared according to the literature [17]. THF was dried and distilled from sodium benzophenone under N<sub>2</sub>. Ethanol was dried with a small amount of clean sodium and distilled under N<sub>2</sub>. De-ionized H<sub>2</sub>O and D<sub>2</sub>O (Cambridge Isotopes, Aldrich) were vigorously deoxygenated with a nitrogen gas stream for a minimum of 2 h and further degassed under vacuum. Other solvents were reagent grade and were deoxygenated by an argon or nitrogen purge prior to use. Triphenylphosphine trisulfonate (TPPTS) was donated by István Horváth from Exxon Research and Engineering Co. All other reagents were commercially obtained and used as received<sup>3</sup>.

<sup>1</sup>H spectra were recorded on a General Electric QE-300 at 300.15 MHz, referenced to DSS in H<sub>2</sub>O/D<sub>2</sub>O and TMS in other solvents. <sup>31</sup>P-NMR spectra were recorded on a Nicolet NC 360 WB instrument operating at 145.33 MHz using a modified version of FELIX (Hare Re-

<sup>1</sup> A phosphine similar to DHPPrPE has been prepared [9] and its coordination chemistry investigated by our laboratory.

<sup>2</sup> See [3,5] and references therein.

<sup>3</sup> Safety note: 1,2-bis(phosphino)ethane (STENCH!) is highly toxic and pyrophoric. Well ventilated lab space and good fume hoods are needed to handle this material safely.

search) for acquisition and processing. Signals were referenced to external 1%  $\text{H}_3\text{PO}_4$ . Samples from the organic phase in the catalytic runs were analyzed by a Shimadzu GC 9A, operating with a  $1/8'' \times 12'$  column of 80/100 mesh activated alumina. Elemental analyses were performed by E and R Microanalytical Laboratory, Corona, NY.

## 2.2. General procedure for hydrogenation reactions

Hydrogenations were carried out in Fisher–Porter bottles with  $20 \times 150$  mm test tube liners. The pressure head consisted of a gauge and two needle valves that were used for filling and depressurizing the bottle. Hydrogen gas was pre-purified by passing it through a Supelco OxyTrap. A stock solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  in THF was prepared to ensure consistent amounts of Rh in all reactions. An appropriate amount of the ligand was dissolved in 6 ml of solvent (usually water) and added to an aliquot of the  $\text{Rh}^{\text{I}}$  stock solution (0.05 mmol, to give a final  $[\text{Rh}^{\text{I}}]$  of 0.007 M) dropwise while stirring. The solution containing the  $\text{Rh}^{\text{I}}$  and the phosphine was allowed to stir for a minimum of 2 h to ensure complete complex formation. Addition of the olefin via pipette was done at this time, or in certain experiments, after the aqueous solution had been heated under  $\text{H}_2$  pressure for 2 h. The pressure tube was slightly evacuated, then purged 10 times with 50 psi of purified  $\text{H}_2$  while shaking to ensure that the solutions were saturated with the gas. Temperatures were kept constant by immersing the Fisher–Porter bottle in an oil bath connected to an Ace Glass temperature controller. The mixtures were stirred magnetically with a Fisher Versamix stirring motor. Catalyst solutions were recycled by physically removing the organic phase with a disposable pipette and removing the remainder of the organic solvent in vacuo. 1 ml of THF was added to restore the original volume and composition of the solution.

## 2.3. Synthesis of 1,2-bis[(dihydroxypropyl)phosphino]ethane (DHP<sub>r</sub>PE)

1,2-Bis(phosphino)ethane (8.0 g, 85 mmol), allyl alcohol (23.0 g, 396 mmol), and VAZO 67 (1.9 g, 10 mmol) were dissolved in 120 ml methanol in a 500 ml round-bottom flask. The flask was sealed with a rubber septum and steel worm clamp<sup>4</sup>. The flask was removed from the glove box and placed in an oil bath at 60°C for 24 h and stirred magnetically. After this time, the reaction mixture was cooled to room temperature and brought into the glove box. The solvent was removed under vacuum until about 50 ml remained. With vigorous stirring, 400 ml of anhydrous diethyl ether was added, forming a white precipitate. The precipitate was collected on a fritted glass funnel, rinsed with 200 ml of diethyl ether, and then dried in vacuo. (Yield: 81%). Anal. calcd. for  $\text{C}_{12}\text{H}_{32}\text{O}_4\text{P}_2$ : C, 51.52; H, 9.88; P, 18.98; Found: C, 51.79; H, 9.97; P, 18.76. <sup>1</sup>H-NMR  $\delta(\text{D}_2\text{O})$ : 1.52 (m, br, 8H,  $4 \times \text{P}-\text{CH}_2$ ), 1.57 (m, br, 4H,  $\text{P}-\text{CH}_2\text{CH}_2-\text{P}$ ), 1.64 (m, br, 8H,  $4 \times \text{CH}_2$ ), 3.61 (t, 8H,  $4 \times \text{CH}_2-\text{OH}$ ), 4.8 (s, OH). <sup>31</sup>P-NMR  $\delta(\text{D}_2\text{O})$ : -27.3 (s).

## 2.4. Synthesis of 1,2-bis[(disodiumsulfonatopropyl)phosphino]ethane (DSP<sub>r</sub>PE)

This ligand was prepared by the procedure above, except as follows. 1,2-Bis(phosphino)ethane (3.0 g, 32 mmol), allyl sulfonic acid sodium salt (20.0 g, 139 mmol), and VAZO 67 (1.5 g, 8 mmol) were slurried in 150 ml methanol in a 500 ml round-bottom flask. The flask was sealed, removed from the glove box and then heated at 60°C for 48 h. The reaction mixture was cooled to room temperature and brought into the glove box. The white precipitate was collected on a fritted glass funnel, rinsed with five 100 ml washes of hot

<sup>4</sup> Safety note: Because round-bottom flasks are not designed to handle high pressures, it is recommended that the temperature in the flask not exceed 60°C. Use a blast shield for this procedure.

methanol to remove unreacted allyl sulfonic acid sodium salt, and then dried in vacuo. (Yield: 70%). Anal. Calcd for  $C_{12}H_{28}Na_4O_{12}P_2S_4$ : C, 25.08; H, 4.21; P, 9.24; S, 19.13 Found: C, 25.14; H, 4.42; P, 9.32; S, 19.00.  $^1H$ -NMR  $\delta(D_2O)$ : 1.65 (m br, 12H,  $6 \times P-CH_2$ ), 1.87 (m br, 8H,  $4 \times CH_2$ ), 2.99 (t, 8H,  $4 \times CH_2-SO_3Na$ ).  $^{31}P$  NMR  $\delta(D_2O)$ :  $-27.7$  (s).

### 2.5. Characterization of $[Rh^I(COD)(DHPPrPE)]Cl$

A solution of DHPPrPE (0.111 g, 0.34 mmol) in 5 ml of  $H_2O$  was slowly added to a stirred solution of  $[Rh(COD)Cl]_2$  (0.085 g, 0.17 mmol) in THF at room temperature. The yellow solution was stirred for 1 h and then evacuated to dryness to yield an orange–yellow glass. The solid was dissolved in 5 ml of water, filtered, and precipitated with 30 ml of THF. The yellow product was filtered and then dried in vacuo. (Yield: 70% based on DHPPrPE).  $^1H$ -NMR  $\delta(D_2O)$ : 1.7 (m, br, 12H,  $6 \times P-CH_2$ ), 2.0 (m, br, 8H,  $4 \times CH_2$ ), 2.44 (s, 8H,  $4 \times CH_2(COD)$ ), 3.59 (t, 8H,  $4 \times CH_2OH$ ), 4.8 (s, OH), 5.2 (s, 4H,  $4 \times CH(COD)$ ).  $^{31}P$ -NMR  $\delta(D_2O)$ : 56.7, 57.7 (d,  $J_{RhP} = 138$  Hz).

### 2.6. Synthesis of $[Rh^I(DHPPrPE)_2]Cl$

DHPPrPE (0.110 g, 0.34 mmol) in 10 ml of ethanol was added to  $[Rh(COD)Cl]_2$  (0.041 g, 0.083 mmol). The yellow solution was stirred for 3 h and was then evacuated to dryness to yield an oily orange solid. The solid was partially dissolved in 10 ml of water, filtered, and dried in vacuo. Further drying of the oily solid may be accomplished by successive extractions with acetone to give a yellow powder. (Yield: 82% based on DHPPrPE). X-Ray quality crystals were obtained by layering an ethanol solution of the complex with THF and cooling at  $-40^\circ C$ .  $^1H$  NMR  $\delta(D_2O)$ : 1.7 (m, br, 24H,  $6 \times P-CH_2$ ), 1.9 (m, br, 16H,  $4 \times CH_2$ ), 3.59 (t, 16H,  $4 \times CH_2OH$ ), 4.8 (s, OH).  $^{31}P$  NMR  $\delta(D_2O)$ : 56.2, 57.1 (d,  $J_{RhP} = 130$  Hz).

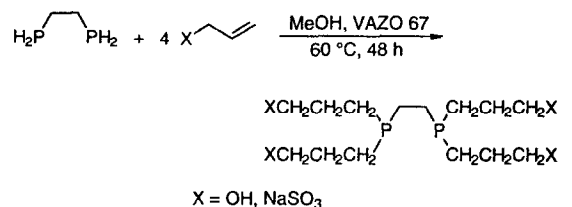
### 2.7. Characterization of 1,2-bis[(dihydroxypropyl) phosphino]ethane dioxide

A solution of DHPPrPE (40 mg, 0.12 mmol) in 1 ml of  $D_2O$  was prepared in an NMR tube sealed with a J. Young valve and covered with a rubber septum. 0.1 ml of a 15%  $H_2O_2$  solution was syringed into the NMR tube. The  $^{31}P$ -NMR spectrum showed a singlet at 59.3 ppm.

## 3. Results and discussion

### 3.1. Ligand synthesis

Two new water-soluble phosphine ligands, DHPPrPE and DSPrPE, were prepared in high yields by using a water-soluble radical initiator to initiate the free radical addition of either allyl sulfonic acid (sodium salt) or allyl alcohol to 1,2-bis(phosphino)ethane (Eq. (1)).



(1)

Isolation of  $> 95\%$  pure (by NMR) material is readily accomplished with minimal product workup, and higher purity materials may be obtained with further recrystallization/precipitation. DSPrPE is very soluble in water, up to and possibly in excess 1 g in 1 ml (1.5 M), but it is practically insoluble in polar organic solvents. DHPPrPE is also soluble to 1 g/ml in water, but it is dramatically more soluble than DSPrPE in polar organics such as alcohols. No degradation of either ligand appeared to take place in aqueous solutions over the course of several weeks. Although the ligands are air-sensitive, brief exposure to air does not lead to detectable amounts of phosphine oxides or other decomposition products.

### 3.2. Synthesis and X-ray structure of $[Rh^I(DHPrPE)_2][Cl]$

Transition metal complexes of the two new ligands are also quite soluble in water. In fact, in some cases the complexes with DHPrPE are qualitatively more soluble than the DHPrPE ligand itself. For DHPrPE, the complexes of  $Rh^I$  are prepared in moderate to high yields in water or polar organic solvents using the readily available  $[Rh(COD)Cl]_2$  complex. Orange, cubic crystals of  $[Rh^I(DHPrPE)_2][Cl]$  suitable for an X-ray diffraction study were grown from ethanol/THF. The X-ray structure shows the expected square planar geometry at the  $Rh^I$  center, with a slightly puckered 1,2-bis(diphosphino)ethane ligand (Fig. 1) [18]. This geometry about the metal center dictates the pseudo-axial positioning of the alkylhydroxy side chains. An extensive system of hydrogen bonds involving all hydroxyl groups is inferred from the shorter  $O \cdots Cl$  distances [3.04–3.38(1) Å] and interanion  $O \cdots O$  distances [2.69–2.78(1) Å]. In addition, there may be intramolecular hydrogen bonding between the alkylhydroxy groups, as evidenced by the broad NMR lines and slight disorder in the crystal structure. Unfortunately, repeated attempts at crystallization of DSPrPE and its transition metal complexes were unsuccessful.

### 3.3. Biphasic hydrogenation catalysis

In order to determine the general effectiveness of DHPrPE and DSPrPE in biphasic catalytic reactions, we investigated the hydrogenation of simple olefins with  $Rh^I$  complexes. The results are summarized in Table 1. Our initial finding was that complexes of the formula  $[Rh^I(diphosphine)_2]Cl$  were practically inactive towards the hydrogenation of alkenes such as cyclohexene and 1-hexene (entries 1, 2, and 9). Fewer than 5 turnovers (TON) were seen in biphasic reactions run at 50 psi  $H_2$  and 60°C for 48 h. A single-phase reaction of the  $[Rh^I(diphosphine)_2]Cl$  in methanol/hexene produced similar results. The lack of easily accessible *cis*

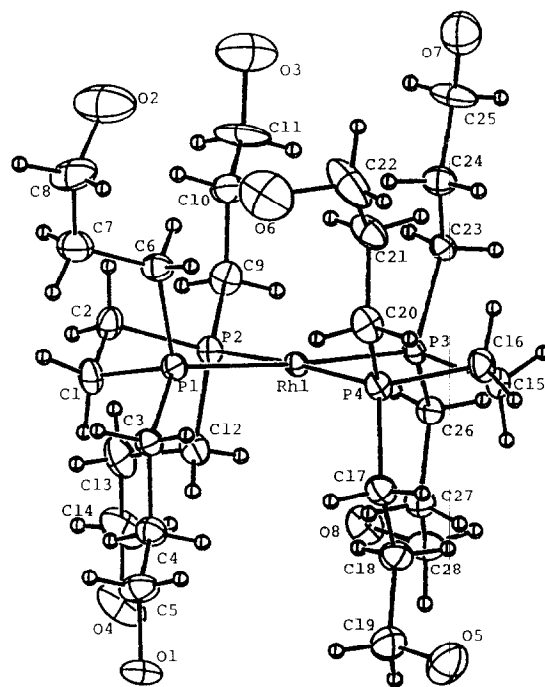


Fig. 1. X-Ray crystal structure of  $[Rh(DHPrPE)_2][Cl]$ . Key bond lengths:  $Rh(1)-P(1)$  2.296(2),  $Rh(1)-P(2)$  2.292(2),  $Rh(1)-P(3)$  2.278(2),  $Rh(1)-P(4)$  2.283(2) Å. Key bond angles:  $P(1)-Rh(1)-P(2)$  83.24(7),  $P(1)-Rh(1)-P(3)$  175.65(8),  $P(1)-Rh(1)-P(4)$  96.01(8),  $P(2)-Rh(1)-P(3)$  96.13(8)°.

coordination sites for  $H_2$  and the olefin on the *trans*  $[Rh^I(diphosphine)_2]^+$  complex (Fig. 1) explains the low activity.

In contrast to the results above with the  $[Rh^I(diphosphine)_2]^+$  complexes, solutions with a DSPrPE:rhodium molar ratio of 1.5:1 were effective in the hydrogenation of 1-hexene. In reactions run at 60°C and 50 psi  $H_2$ , a complete conversion of the olefin to n-hexane was observed by GC analysis after 19 h (entry 3). This corresponds to a total of 480 TON, or 25 TOF (TON/h). Lower conversions are seen at lower temperatures and shorter reaction times, as well as some isomerization to internal 2- and 3-hexenes.

In a direct comparison with the activity of  $Rh(TPPTS)_3Cl$ , the system with 1.5 eq. of DSPrPE had a TON three times higher than the TPPTS system at room temperature (entry 7, 8). The higher activity of DSPrPE may be due to a pronounced surfactant ability, as this may en-

Table 1

Results from the hydrogenations of alkenes with Rh<sup>I</sup> complexes of DSPrPE and DHPPrPE <sup>a</sup>

Entry	Ligand	T (°C)	Eq.	Substrate	Time (h)	Conversion (TON)
1	DSPrPE	60	2	1-Hexene	48	0.5% (2)
2	DSPrPE	60	2	Cyclohexene	48	1% (4)
3	DSPrPE	60	1.5	1-Hexene	19	100% (480)
4	DSPrPE <sup>b</sup>	60	1.5	1-Hexene	19	69% (332)
5	DSPrPE	60	1.5	Crotonaldehyde	60	100% (975)
6	DSPrPE <sup>b</sup>	60	1.5	Crotonaldehyde	26.5	56% (550)
7	DSPrPE	20	1.5	1-Hexene	10	12% (58)
8	TPPTS	20	3	1-Hexene	10	3.5% (17)
9	DHPPrPE	60	2	1-Hexene	48	0.5% (2)
10	DHPPrPE	60	1.5	1-Hexene	5	<sup>c</sup>
11	DHPPrPE	20	1.5	1-Hexene	5	<sup>c</sup>
12	DHPPrPE	20	1.5	1-Hexene	5	<sup>c,d</sup>
13	DHPPrPE	20	1.5	1-Hexene	5	<sup>c,e</sup>
14	DHPPrPE	20	1.5	1-Hexene	5	<sup>c,f</sup>
15	DHPPrPE <sup>g</sup>	60	1.5	1-Hexene	16	10% (48)
16	DSPrPE <sup>g</sup>	60	1.5	1-Hexene	16	22% (106)

<sup>a</sup> Complexes prepared from [Rh<sup>I</sup>(COD)Cl]<sub>2</sub>, Rh<sup>I</sup> 0.05 mmol, 1 ml THF, 6 ml H<sub>2</sub>O, H<sub>2</sub> pressure 50 psi.<sup>b</sup> Recycled aqueous phase.<sup>c</sup> Formation of Rh metal occurred.<sup>d</sup> Addition of 4 eq. Na<sub>2</sub>SO<sub>4</sub>.<sup>e</sup> Complex prepared from Rh<sup>I</sup>(COD)OTf.<sup>f</sup> pH 5 or 10.<sup>g</sup> Aqueous solution preheated under 50 psi H<sub>2</sub> prior to addition of alkene.

hance the solubility of normally hydrophobic hexene [19] <sup>5</sup>. Evidence for this effect was the observation of emulsions which were generally formed in the biphasic reactions with DSPrPE. However, the emulsions dissipated quickly and completely once the stirring was stopped to allow for a clean separation of the two phases. In contrast, only a minimal emulsion was seen in the TPPTS system. Although the actual TONs for entries 7 and 8 appear low, note that only a small amount of THF was used in these experiments as a cosolvent. Other work suggests that other cosolvents, such as alcohols, may give higher TONs [2].

DSPrPE complexes with rhodium also selectively hydrogenate the alkene of crotonaldehyde (entries 5 and 6). Less than 1% of the aldehyde was reduced to crotyl or butyl alcohol, even at 100% conversion of the alkene. The solutions

with both substrates remained homogeneous throughout the catalytic reactions, and all of the yellow color of the Rh<sup>I</sup> complex was in the aqueous phase. <sup>31</sup>P NMR analysis of a concentrated organic phase (hexene/hexane) detected no free or coordinated phosphine species after a 24 h reaction period.

Attempts to recycle the catalyst solutions using DSPrPE gave mixed results. Aqueous solutions were physically separated from the organic phase and were then placed under vacuum to remove residual dissolved organics. Because the original solutions consisted of 1 ml of THF, this was added to the aqueous solution along with a new aliquot of 1-hexene. The activity of the recycled catalyst was always lower than that of the original solutions (entry 4), but the degree of activity was inconsistent. Additions of Hg metal (10 eq.) to the solutions did not decrease activity in reactions with the sulfonated ligand, suggesting that a homogeneous rhodium complex is responsible for the catalytic transformation [20].

<sup>5</sup> See [3] and [13] for discussions of surfactant effects in biphasic catalysis.

Reactions of  $\text{Rh}^I$  complexes with the DHPrPE ligand were not as clean as those with DSPrPE. While solutions of  $[\text{Rh}^I(\text{DHPrPE})_2]\text{Cl}$  remained homogeneous, solutions with a lower ratio of diphosphine to metal would precipitate shiny metallic rhodium. This precipitation would occur regardless of the temperature, although higher temperatures would lead to greater amounts of decomposition. Several reaction variables were altered in order to stabilize the complex (entries 13, 14, 15). Initially, it was thought that some of the ligand might be extracted into the organic phase, but precipitation of the metal occurred even when the reactions were run homogeneously in methanol/hexene. Increasing the reaction time for the complex formation from 2 to 12 h also had no effect. Using the triflate salt of  $\text{Rh}^I(\text{COD})^+$  instead of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  also led to catalyst decomposition [21]. In an effort to approximate more closely the conditions of the catalyst solutions of DSPrPE, 4 eq. of sodium sulfate was added to the aqueous catalyst solution, again with no effect. Consideration of the phosphine basicity led us to alter the pH of the solution between 5 and 10, but none of the pH changes stabilized the system. In most of these reactions, the metallic rhodium was accompanied by insoluble brown precipitate, suggesting degradation of the phosphine as well.

In an attempt to promote the formation of a stable catalyst precursor, a solution of  $[\text{Rh}^I(\text{DHPrPE})_{1.5}]\text{Cl}$  in pH 8  $\text{H}_2\text{O}$  was heated for 2 h at  $60^\circ\text{C}$  under 50 psi  $\text{H}_2$  pressure. The solution remained clear yellow, and subsequent addition of 1-hexene produced a system that would hydrogenate 10% of the olefin (48 TON) after 10 h at 50 psi  $\text{H}_2$  and  $60^\circ\text{C}$  (entry 15). While this TON is significantly lower than that of the DSPrPE system described above, it was the first set of conditions that allowed for the apparent homogeneous biphasic catalysis with the DHPrPE ligand<sup>6</sup>. In a direct comparison,

<sup>6</sup> Note that the addition of elemental Hg (10 eq.) did not reduce the amount of hexane produced.

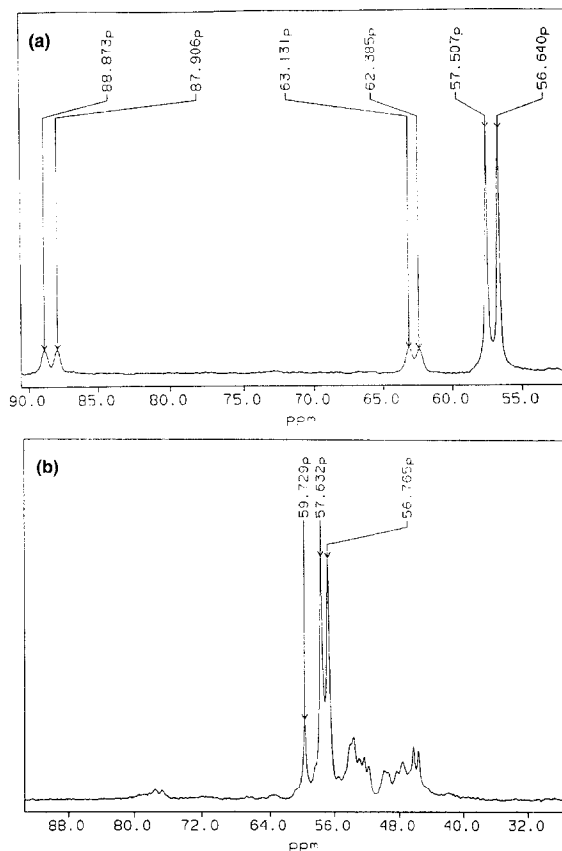


Fig. 2. (a)  $^{31}\text{P}$ -NMR spectrum of catalyst solution after 2 h pretreatment; (b) after solution used for hydrogenation of 1-hexene.

the DSPrPE system yielded 22% conversion (105 TON) under these conditions (entry 16). Again, this increased activity for DSPrPE over that of DHPrPE may be due to its enhanced surfactant properties<sup>7</sup>.

Analysis of the rhodium–diphosphine complex after 2 h of preheating under  $\text{H}_2$  pressure showed a series of new doublets in the  $^{31}\text{P}$ -NMR spectrum (Fig. 2a). Two sets of doublets at 88 and 63 ppm are clearly seen, while another doublet may be present at 53 ppm. We are unsure of the significance of these species, however, as Fig. 2b shows that these species are not present after the solution has been used in a hydrogenation reaction. Some phosphine oxide may be present (s,  $\delta$  59.7 ppm) as well as an unidentified species (d,  $\delta$  46 ppm). The major

<sup>7</sup> Note that no emulsions were seen in DHPrPE solutions.

species present is the starting complex (d,  $\delta$  57 ppm). Investigation of the unknown species is currently in progress.

#### 4. Conclusions

Two new, water-soluble, chelating alkyl phosphines were synthesized. The syntheses provide pure materials, free from unreacted starting materials and oxidation products. The coordination chemistry of the ligands with a common rhodium(I) precursor conforms to the expected behavior of other 1,2-bis(diphosphino)ethane compounds. While the DHPPrPE ligand is less effective in hydrogenations than its sulfonated equivalent, it can be of value due to its solubility in a wider range of solvents. Rhodium complexes with DSPrPE can hydrogenate alkenes completely and selectively, and at a higher activity than a similar system prepared with TPPTS.

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