Pergamon

Tetrahedron 56 (2000) 7093–7097

TETRAHEDRON

# A Synthetic Route to a New Surface-Active Phosphine Ligand: 12-DPDP (12-Diphenylphosphinododecylphosphonate)

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Received 29 January 2000; accepted 15 June 2000

**Abstract**—A water-soluble phosphonate-functionalized phosphine ligand $Na_2[Ph_2P(CH_2)_{12}PO_3]$ (**8**), was prepared in eight steps from cyclododecanone. Phosphine **8** reacts with $[Rh(COD)Cl]_2$ in methanol to give the new complex $Na_2[Rh(COD)(Ph_2P(CH_2)_{12}PO_3)Cl]$ (**9**). Complex **9** is inactive in the catalytic hydrogenation of 1-hexene and cyclohexene due to the decomposition of **9** to rhodium metal in the presence of hydrogen gas. Hydrogenation of decene using $[Rh(COD)_2]BF_4$ and 3 equiv. of **8** in an aqueous emulsion was achieved using 1 atm $H_2$. $^{31}P$ NMR studies on **8** suggest a lack of well-defined aggregation in water, which has been ascribed to the steric bulk of the diphenylphosphino group. 

## Introduction

The field of aqueous and biphasic homogeneous catalysis has been dominated by the hydrophilic sulfonated phosphine, TPPTS ('triphenylphosphine trisulfonate'). Early work on the use of TPPTS in aqueous phase hydroformylation and hydrogenation has spurred intense interest in applying the technique to alternative homogeneous transition metal reactions such as Suzuki coupling, allylic substitution, hydrodimerization and aqueous enantioselective catalysis.[1,2] The attraction of using water as a solvent is obvious from the environmental aspect, but a further advantage is the easy separation of the water-soluble catalyst from water-insoluble organic products. The limitation of low aqueous solubility for the majority of organic compounds may be circumvented by using either a biphasic organic–aqueous system where reactivity takes place at the interface, or the addition of a polar organic co-solvent to allow adequate partitioning of reactants, products and catalyst. The solubility of substrates may also be increased by adding a suitable surfactant which solubilizes hydrophobic organic compounds, and additional potential benefits such as the increase in catalytic reaction rates and improvements in selectivities (regio-selective and enantioselective) have been suggested and realized in a few isolated cases.[3] If the correct surfactant system is chosen, metal complexes may form part of a discrete aggregate structure such as a micelle or a bilayer, and the possibility of micro-environmental control of the catalytic transition metal centers becomes viable. As such, micellar micro-reactors are related to the new catalytic systems based on metallo-dendrimers which are currently in vogue.[4]

As part of our on-going research into the use of water-soluble organometallic compounds in aqueous phase homogeneous catalysis, we have recently investigated the transition metal coordination chemistry of the highly water-soluble, phosphonylated phosphine, TPPMP ('triphenylphosphine monophosphonate') in the aqueous phase.[5] We have also reported the use of TPPMP as a ligand in the palladium catalyzed carbonylation of benzyl halides in water.[6]

## Experimental

### General data

All reactions were conducted under dry, pre-purified $N_2$ using standard Schlenk-line and catheter-tubing techniques unless otherwise stated. IR spectra were recorded on a Mattson Galaxy 6020 (FT) spectrometer. All $^1H$ and $^{31}P$ NMR spectra were recorded on a Bruker AC-300 spectrometer and referenced to internal tetramethylsilane or residual $CHCl_3$ ($^1H$), and external $H_3PO_4$ ($^{31}P$). Mass spectra were recorded on a Hewlett–Packard 5971A/5870 GC-mass spectrometer equipped with a 20 m×0.22 mm HP fused silica column, with a stationary phase of cross-linked 5% phenylmethylsilicone, or were performed by Mass Consortium, San Diego, CA.

Solvents were purified as follows: THF and ether, distilled

*Keywords*: phosphine; amphipathic; rhodium; phosphonate.

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0040–4020/00/$ - see front matter 
PII: S0040-4020(00)00546-9

from sodium/benzophenone; hexane, hexanes and $CH_2Cl_2$, distilled from $CaH_2$; ethyl acetate, methanol, acetone, acetic acid (Fisher), ethanol (Aaper Alcohol and Chemical Co.), anhydrous DME (Aldrich), $CDCl_3$, acetone-$d_6$ and $D_2O$ (Cambridge Isotope Laboratories), used as received. Silica gel (Scientific Products, 230–400 mesh), magnesium sulfate and sodium sulfate (Fisher) were used as received.

Reagents were obtained as follows: cyclohexene, 1-hexene, 1-decene, 2,4,6-collidine, sodium dodecyl sulfate, trityl chloride, sodium hydroxide (Aldrich), hydrogen (MG Industries), 10% palladium–charcoal (MC&B), sodium borohydride, tetraethylammonium perchlorate (Fluka), $TiCl_4$, perchloric acid, hydriodic acid, triethylamine (Fisher), $LiPPh_2$, prepared according to Ref. 21; *p*-toluenesulfonyl chloride (Aldrich), recrystallized before use; di-*n*-butylphosphosphite (Aldrich), vacuum distilled prior to use; *m*-CPBA was purified according to the literature procedure.[7] $[Rh(COD)_2]BF_4$ was synthesized according to the literature procedure.[8]

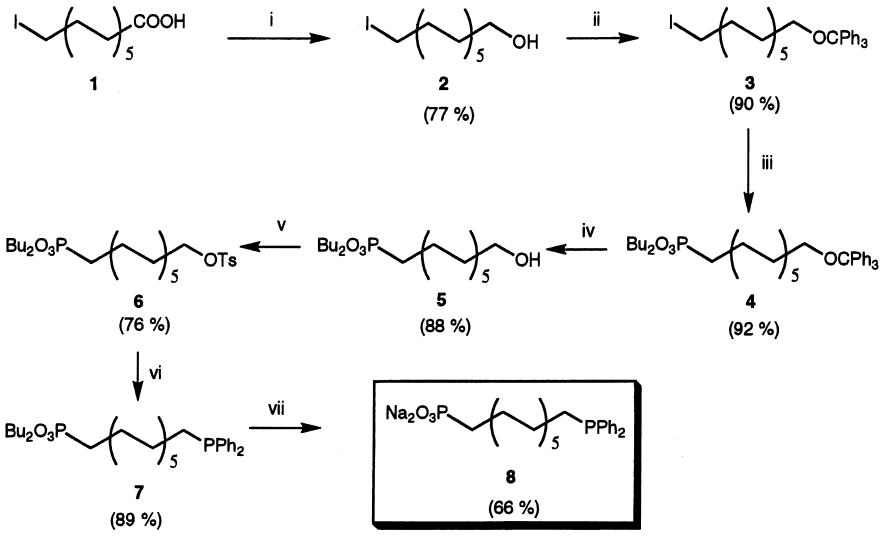
**12-Iodododecan-1-oic acid (1).** A 500 mL flask was charged with cyclododecanone (27.35 g, 0.1500 mol), *m*-CPBA (43.97 g, 0.255 mol) and $CH_2Cl_2$ (200 mL). Then, trifluoroacetic acid (0.12 mL, 1.5 mmol) was added and the mixture was refluxed for 45 h. The reaction was allowed to cool to room temperature and the resulting white solid was filtered off. The filtrate was diluted with $CH_2Cl_2$ (800 mL), washed successively with $K_2CO_3$ solution (2×250 mL), water (250 mL) and sodium thiosulfate solution (250 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent removed via rotary evaporation. The residue was dissolved in 95% EtOH (100 mL) and $NaBH_4$ (0.378 g, 0.010 mmol) in EtOH (10 mL) was added and the reaction mixture was stirred for 30 min. Then, 1 M hydrochloric acid solution (100 mL) and ether (200 mL) were added. Solvent was removed from the organic phase via rotary evaporation and the resulting residue was transferred to a 500 mL round-bottom flask equipped with a reflux condensor and stirrer bar. Hydriodic acid (100 mL, 0.76 mol, 57%) was added via syringe and immediately followed by acetic acid (100 mL). The solution was refluxed for 3 h during which time the color changed from orange to pale yellow. The solution was allowed to cool to room temperature and separated into two phases. The mixture was poured onto water (1000 mL) and a precipitate immediately formed, which was collected by filtration, air-dried and then dried under oil-pump vacuum. Crystallization from hexanes (300 mL) gave **1** as pink flakes (30.85 g, 63%), mp 69–71°C. IR (KBr disk): $\nu$(C═O) 1691 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 3.19 (t, 2H, $ICH_2$–), 2.35 (t, 2H, $HO_2CCH_2$–), 1.82 (m, 2H, $HO_2CH_2CH_2$–), 1.63 (m, 2H, $ICH_2CH_2$–), 1.45–1.25 (m, 14H, $CH_2$). MS (EI-MS): *m*/*e* 199 (100%) (M −127).

**12-Iodododecan-1-ol (2).** A 1 L three-neck, round-bottom flask was equipped with a mechanical stirrer, septum and a pressure-equalized dropping funnel. The flask was charged with sodium borohydride (11.45 g, 0.3030 mol) and anhydrous DME (350 mL). The flask was then cooled in an ice bath and $TiCl_4$ (11.1 mL, 0.101 mol) was added via syringe. Then, a solution of **1** (30.00 g, 92.00 mmol) in anhydrous DME (150 mL) was added via a dropping funnel over a period of 20–30 min. The ice-bath was removed and the mixture stirred overnight at room temperature. The reaction mixture was cooled to 0°C (ice-bath) and water was carefully added (375 mL). The reaction mixture was then poured into ether (500 mL) and the two phases separated. The aqueous phase was washed with ether (200 mL) and the organic fractions combined and dried over anhydrous $Na_2SO_4$. Then, the ether solution was concentrated using rotary evaporation to give a yellow oil which solidified on standing. The residue was taken up in hexane and chromatographed on a 50 mm diameter column (179 g silica gel, ether–hexane). The solvent was removed from the eluate to give **2** as spectroscopically pure colorless oil (22.01 g, 77%). IR (NaCl, thin film): $\nu$(O–H) 3321 $cm^{-1}$, $\nu$(C–O) 1051 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 3.64 (t, 2H, $HOCH_2$–), 3.19 (2H, t, $ICH_2$), 1.82 (m, 2H, $HOCH_2CH_2$–), 1.63–1.23 (m, 20H, $CH_2$).

**12-Iodododecan-1-ol trityl ether (3).** A 250 mL Schlenk flask was equipped with magnetic stirrer bar and charged with **2** (15.61 g, 50.00 mmol), trityl chloride (13.94 g, 50.00 mmol), and $Et_4NClO_4$ (11.49 g, 50.00 mmol) and $CH_2Cl_2$ (200 mL). Then, 1.5 equiv. of 2,4,6-collidine (9.9 mL, 7.5 mol) was added via syringe and the solution was stirred for ca. 30 min. Water (200 mL) was added and the two phases were separated. The organic phase was washed with water and dried over anhydrous $MgSO_4$. Then, the solution was concentrated using rotary evaporation and the resulting oil chromatographed on a 50 mm diameter column (201 g silica gel, ether–hexane). The solvent was removed from the eluate to give **3** as an orange oil (24.30 g, 90%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.54–7.16 (m, 15H, $3C_6H_5$), 3.17 (2H, t, $ICH_2$), 3.03 (2H, t, $CH_2OC$–), 1.80 (m, 2H, $ICH_2CH_2$–), 1.61 (m, 2H, C–$OCH_2CH_2$–), 1.44–1.06 (m, 18H, $CH_2$).

**12-Di-*n*-butylphosphonododecan-1-ol trityl ether (4).** A 500 mL Schlenk flask was equipped with a mechanical stirrer, pressure-equalizing addition funnel, reflux condenser and charged with sodium metal (1.27 g, 55.0 mmol) and hexane (125 mL). The mixture was heated to reflux and a solution of di-*n*-butylphosphite (10.7 mL, 55.0 mmol) in hexane (25 mL) was added dropwise with stirring. The mixture was refluxed overnight and then allowed to cool to room temperature. A solution of **3** (21.45 g, 39.50 mmol) in hexane (50 mL) was added dropwise. The mixture was refluxed overnight, allowed to cool to room temperature and quenched with 10% NaCl solution (100 mL). Ether (100 mL) was added and the two phases separated. The organic phase was washed with a portion of 10% NaCl solution (100 mL) and the aqueous phase extracted with ether (100 mL). The ether fractions were combined, dried (anhydrous $Na_2SO_4$) and solvent removed on a rotary evaporator. The resulting residue was chromatographed on a 50 mm diameter column (150 g silica gel, ethyl acetate). The solvent was removed from the eluate to give **4** as a pale yellow oil (22.64 g, 92%). IR (NaCl, thin film): $\nu(PO_3)$ 1071, 1026, 1003, 978 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.30–7.50 (m, 15H, $3C_6H_5$), 4.05 (m, 4H, $2CH_2OP$) 3.05, (2H, t, $CH_2OC$–), 1.80–1.20 (m, 22H, $CH_2$), 0.93 (t, 6H, $2CH_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 33.3 (s).

**12-Di-*n*-butylphosphonododecan-1-ol (5).** A 1 L Parr




**Scheme 1.** *Reagents and conditions:* (i) $NaBH_4$, $TiCl_4$; (ii) $Ph_3CCl$, $Et_4N^+ ClO_4^-$, 2,4,6-collidine; (iii) Na, HP(O) $(OBu)_2$; (iv) $H_2$, Pd–C, $HClO_4$; (v) TsCl, $Et_3N$, 0°C; (vi) $LiPPh_2$, −78°C; (vii) $Me_3SiBr$, $H_2O$, NaOH.

bomb was charged with a solution of **4** (22.54 g, 36.30 mmol), 70% perchloric acid (1 mL) in 95% ethanol (200 mL) and a stirrer bar. The bomb was flushed with $N_2$ and 10% Pd/C (3.38 g, 15 wt%) was added. The bomb was pressurized with 60 psi hydrogen and the solution stirred for 16 h. Then the reaction mixture was filtered though a pad of Celite and the solvent removed on a rotary evaporator. The resulting residue was chromatographed on a 50 mm diameter column (144 g silica gel, methanol–$CH_2Cl_2$). The solvent was removed from the eluate to give **5** as a pale yellow oil (12.03 g, 88%). IR (NaCl, thin film): $\nu$(O–H) 3420 $cm^{-1}$, $\nu(PO_3)$ 1067, 1024, 981 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.01 (m, 4H, $2CH_2OP$) 3.62, (2H, t, $CH_2OC$–), 1.79–1.20 (m, 32H, $16CH_2$), 0.94 (t, 6H, $2CH_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 33.3 (s).

**12-Di-*n*-butylphosphonododecan-1-tosylate (6).** A 100 mL Schlenk flask was charged with **5** (2.026 g, 5.000 mmol), $CH_2Cl_2$ (20 mL) and a stirrer bar, and cooled to 0°C (ice bath). Then, *p*-toluenesulfonyl chloride (1.122 g, 6.000 mmol) and $Et_3N$ (0.89 mL, 6.4 mmol) were added, the cold bath was removed and the reaction mixture was stirred overnight. A solution of 1 M HCl was added and the organic layer was separated and washed with aqueous $NaHCO_3$, water and dried over anhydrous $Na_2SO_4$. The solvent was removed on a rotary evaporator and the resulting residue was chromatographed on a 20 mm diameter column (25 g silica gel, ether–hexane). The solvent was removed from the eluate to give **6** as a yellow oil (2.19 g, 76%). IR (NaCl, thin film): $\nu(PO_3)$ 1097, 1068, 1024, 976 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.55 (dd, 4H, $C_6H_4$), 4.05 (m, 4H, $2CH_2OP$), 2.46 (s, $ArCH_3$), 1.85–1.15 (m, 32H, $16CH_2$), 0.95 (t, 6H, $2CH_2CH_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 33.3 (s). MS (ES-MS): *m/e* 379 ($MH^+$).

**12-Di-*n*-butylphosphonododec-1-yldiphenylphosphine (7).** A 100 mL Schlenk flask was charged with **6** (1.86 g, 3.49 mmol), THF (25 mL), a stirrer bar, and cooled to −78°C ($CO_2$/*i*-propanol). Then a solution of $LiPPh_2$ (4.0 mL, 4.0 mmol, 1 M in THF) was added via syringe with stirring. The reaction was stirred for 1 h and the cold bath removed. The reaction was allowed to warm to room temperature and the solvent was removed under oil-pump vacuum. Dichloromethane (2×25 mL) was added and the suspension chromatographed on a 20 mm diameter column (50 g Florosil, $CH_2Cl_2$–THF). The solvent was removed from the eluate to give **7** as a pale yellow oil (1.704 g, 89%). IR (NaCl, thin film): $\nu(PO_3)$ 1068, 1024, 1001, 978 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.8–7.2 (m, 10H, $2C_6H_5$), 4.05 (m, 4H, $2CH_2OP$), 1.95–1.20 (m, 32H, $16CH_2$), 0.95 (t, 6H, $2CH_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 33.3 (s, PO), −15.5 (s, P).

**12-Diphenylphosphinododecylphosphonate disodium salt $Na_2$[12-DPDP] (8).** A 100 mL Schlenk flask was charged with **7** (1.70 g, 3.10 mmol), $CH_2Cl_2$ (20 mL) and a stirrer bar. Then bromotrimethylsilane[9] (1.6 mL, 12 mmol) was added via syringe with stirring. The reaction was stirred for 4 h and the solvent was removed under oil-pump vacuum. A solution of water (0.23 mL, 13 mmol) in acetone (10 mL) was added and the solution was stirred for a further 20 min. The solvent was removed under oil-pump vacuum and the residue was taken up in MeOH (10 mL). A Schlenk tube was charged with sodium hydroxide (0.258 g, 6.45 mmol) and water (1.0 mL) and the resulting solution was transferred via cannula to the methanolic solution of 12-DPDP. The solvent was removed under oil-pump vacuum and THF (30 mL) and added to the resulting residue and stirred for several minutes. The resulting white suspension was filtered to give a white solid which was extracted with methanol and the solvent removed under oil-pump vacuum to give **8** as a white solid (0.986 g, 66%). IR (KBr): $\nu$(O–H) 3406 $cm^{-1}$, $\nu$(C–H) 2922, 2851 $cm^{-1}$, $\nu$(P–O) 1066 $cm^{-1}$. $^{31}P$ NMR ($CDCl_3$): $\delta$ 25.5 (s, PO), −15.4 (s, P).

## Synthesis of $Na_2$[12-DPDP]

The synthetic route to $Na_2$[12-DPDP] was largely dictated by consideration of the cost of starting materials and reagents, but there was a conscious decision to develop the chemistry of α,ω-functionalized alkanes where the endgroups are chemically distinct. All attempts to sequentially introduce the phosphonate and phosphine groups

using the traditional methods of the Michaelis–Arbuzov reaction, the action of lithium diphenylphosphide on 1, 12-dibromododecane and the formation of a secondary phosphonium salt[10] either gave poor product yields or were hampered by purification problems. The addition of diphenylphosphine[11] to 1-bromododec-12-ene was avoided due to the lack of a commercial source of the olefin. Synthesis was ultimately accomplished in eight steps from cyclododecanone in 14% overall yield and the synthetic route is shown in Scheme 1. The requisite α,ω-functionalized dodecane was obtained from the Baeyer–Villiger oxidation of cyclododecanone to give an intermediate lactone which was subsequently hydrolyzed, and halogenated using mineral acid to give 12-iododecanoic acid **1**. Several methods were attempted for the oxidation of the ketone, including peroxymonosulfuric acid,[12] peracetic acid,[13] and *m*-chloroperbenzoic acid.[8] The method using peracetic acid (from 30% hydrogen peroxide and acetic acid) or perbenzoic acid gave the best results, however the use of hydrogen peroxide–acetic acid was preferable in terms of operational simplicity. In the subsequent conversion of the lactone to the ω-halogeno acid, it was found that the use of 48% hydrobromic acid in the presence of concentrated sulfuric acid was inferior to 57% HI in acetic acid, which is in agreement with the literature reports.[14] It was found that treatment of the crude lactone with sodium borohydride in ethanol gave a cleaner reaction upon treatment with acid. The borohydride is likely to serve two purposes: destruction of any residual oxidant, and reduction of any remaining ketone to the corresponding alcohol. The removal of residual oxidant is important, as halide ion present in the hydrolysis step can be oxidized to molecular halogen. In the presence of the strong acids, the halogen thus produced can react with enolized carbonyl groups to give α-halocarbonyl compounds. By using sodium borohydride reduction followed by HI–AcOH, acid **1** was obtained in 77% overall yield. Following reduction of **1** to the corresponding alcohol **2** with low-valent titanium (formed in situ from sodium borohydride and $TiCl_4$ in DME),[15] it was necessary to protect the alcohol group prior to introduction of the dibutylphosphonate group. The use of protecting groups introduced by nucleophilic alkylation reactions, e.g. benzyl ethers, seemed inappropriate due to the possibility of self-alkylation involving the iodo group.[16] Under the circumstances a reasonable choice was to introduce a trityl group using freshly prepared trityl chloride[17] and tetraethylammonium perchlorate in collidine to give the trityl ether **3** in 90% yield.[18] The spectroscopic properties (NMR and IR) of **1**–**3** and all subsequent compounds are listed in the Experimental section.

The introduction of the phosphonate group using standard Michaelis–Arbuzov conditions (triethylphosphite in refluxing toluene) gave the resulting phosphonate **4** in 50% yield. This is unacceptably low for the introduction of a protecting group in the middle of a multi-step synthesis. Using the Michaelis–Becker reaction (sodium dibutylphosphite in hexane), **4** was obtained in 92% yield. The $^{31}$P NMR spectrum of **4** contained one resonance at 33.3 ppm which is typical for the dialkyl ester of a phosphonic acid. Cleavage of the trityl either protecting group was achieved by hydrogenolysis over palladium–charcoal, with perchloric acid as a promoter.[19] Introduction of the diphenylphosphino group required conversion of the alcohol **5** into the corresponding tosylate **6**.[20] This is a routine reaction but is worth mentioning that the use of tosyl chloride in dichlormethane in the presence of triethylamine gave superior results to the conventional method of tosyl chloride in pyridine. Reaction of **6** with lithium diphenylphosphide[21] in THF gave the expected product **7** cleanly as evidenced by $^{31}$P NMR: the spectrum of **7** contains only two peaks at −15.5 and 33.3 ppm which correspond to the phosphine and phosphonate moieties, respectively. No evidence for dealkylation of the phosphonate ester by the nucleophilic lithium diphenylphosphide was observed. Complete dealkylation of the phosphonate ester using bromotrimethylsilane in dichloromethane and neutraliztion of the acid using sodium hydroxide gave the desired amphiphilic phosphine 12-DPDP (**8**). As expected, phosphine **8** is highly water-soluble, although careful measurements of solubility were not made. In addition to aqueous solubility, the ligand foams considerable on contact with water indicating its highly surface active properties.

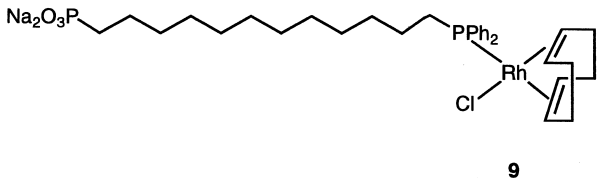
### $^{31}$P NMR studies on $Na_2$[12-DPDP] in solution

The amphipathic nature of 12-DPDP gives rise to the possibility that the ligand could form, or be included in micelles or other aggregate structures such as surface monolayers or lamellar bilayers. The formation of such supramolecular assemblies can have considerable influence the rate or selectivity of an organic reaction. While enantioselectivity has been demonstrated in transition metal catalyzed reactions using reverse micelles,[22] it has also been shown that the microenvironment of the hydrophobic interior of micelles allows for molecular interaction which would otherwise be 'swamped out' by solvent–solute interactions.[23] Physical measurements for determination of the molecular dynamics of amphipathic molecules are numerous. Two of the most common methods are light-scattering and NMR measurements, which can be further divided into chemical shift[24] and relaxometry studies.[25] Before the possibility of aggregation in metal complexes could be investigated, preliminary NMR studies on free 12-DPDP ligand were made. Studies were conducted on 12-DPDP using serial dilutions in degassed water and no significant changes in chemical shift were observed across a wide concentration range (0.01–0.5 M) which could possibly be associated with aggregate formation. In addition, $T_1$ and $T_2$ measurements were inconclusive. No further studies on the aggregation of 12-DPDP were performed and our conclusion is that the bulky hydrophobic diphenylphosphino-group of 12-DPDP is preventing aggregation in aqueous solution and it is unlikely that metal complexes of 12-DPDP will form aggregate structures. Further studies on the use of a co-surfactant such as sodium dodecylsulfate to assist in micelle formation are currently underway.

### Coordination chemistry and catalytic hydrogenation

Preliminary investigations on the coordination of 12-DPDP to a metal center were made. The addition of 2 equiv. of 12-DPDP to a methanolic solution of $[Rh(COD)Cl]_2$ resulted in halide bridge cleavage and the formation of a new rhodium phosphine species in solution as evidenced by $^{31}$P NMR. The $^{31}$P NMR spectrum contained two peaks, a

broad singlet at 26 ppm due to the uncoordinated phosphonate group and a new doublet at 27 ppm which we have assigned to the rhodium coordinated phosphine in complex **9**. The chemical shift and coupling constant ($^1J_{Rh-P}$=154 Hz) are both consistent with this assignment.[26] No other peaks were present in the spectrum.




**9**

The catalytic hydrogenation of a mixture of olefins, 1-hexene and cyclohexene was attempted using compound **9**. An aqueous mixture of both alkenes, along with toluene as an internal standard, was stirred under hydrogen (10 psi) in the presence of 0.1 mol% of **9** at room temperature. Aliquots were taken at 10, 30, 60 and 240 min and analyzed by gas chromatography. No hydrogenation products were detected and the solution had turned black indicating decomposition of the complex. The facile decomposition which explains the lack of catalytic activity for complex **9** is ascribed to the reduction of **9** to rhodium metal and cyclooctane.[26] Successful hydrogenation was achieved however, using 3 equiv. of phosphine ligand per metal center. 12-DPDP and $[Rh(COD)_2]BF_4$ were combined in a 3:1 ratio in water and decene was added as the substrate (catalyst loading: 2.5 mol%, concentration of decene: 6 mmol per 5 ml water). After bubbling hydrogen gas, through the emulsion overnight via a glass frit, analysis of the mixture indicated quantitative reduction of the olefin. Further studies are underway to define the catalytic species present in the emulsion.

## Summary

A new water-soluble surfactant-like phosphine, 12-DPDP, has been synthesized from the inexpensive precursor cyclododecanone in a multi-step sequence. 12-DPDP coordinates to rhodium in the complex [Rh(COD)(12-DPDP)Cl] which is inactive for catalytic hydrogenation of olefins due to the reduction to rhodium metal by molecule hydrogen. An in situ combination of 12-DPDP and $[Rh(COD)_2]BF_4$ in a 3:1 ratio is catalytically active for the hydrogenation of decene.

## Acknowledgements

The donors of the Petroleum Research Fund (PRF 31395-G3) administered by the American Chemical Society are thanked for support of this work. We would also like to thank Dr Todd Johnson for the synthesis of $[Rh(COD)Cl]_2$ and one of the referees for suggestions for the hydrogenation experiment.

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