Synthesis, Reactions, and Catalytic Chemistry of the Water-Soluble Chelating Phosphine 1,2-Bis[bis(*m*-sodiosulfonatophenyl)phosphino]ethane (DPPETS). Complexes with Nickel, Palladium, Platinum, and Rhodium

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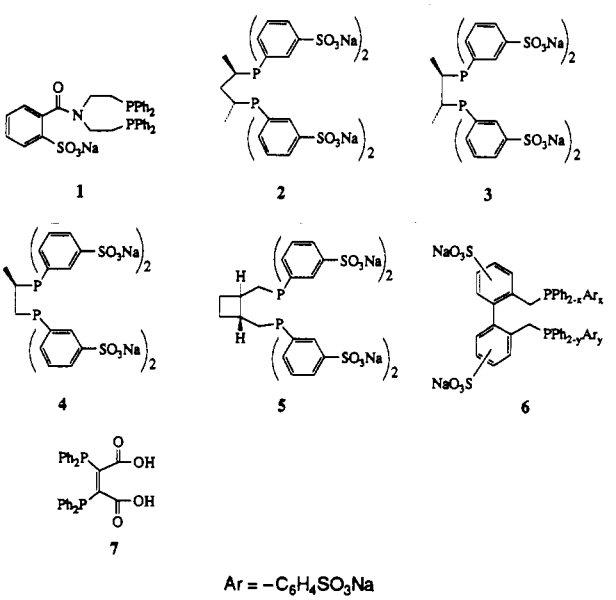
Direct sulfonation of bis(diphenylphosphino)ethane, DPPE, leads to a complicated mixture of sulfonated products which includes 1,2-bis[bis(*m*-sodiosulfonatophenyl)phosphino]ethane, DPPETS. DPPETS is isolated in gram quantities by fractional precipitation; the overall yield is 30%. The ligand is more electron accepting than its nonsulfonated analog, DPPE, as judged by the nickel complexes $Ni(L)(CO)_2$ where L = DPPE and DPPETS. Several coordination compounds of Rh, Pd, and Pt are reported. Water-soluble rhodium compounds prepared in situ from $Rh(acac)(CO)_2$ and DPPETS show poor activity but selectivity similar to that of $Rh(acac)(CO)_2$ + trisulfonated triphenylphosphine in the two-phase hydroformylation of octene-1. Under two-phase reaction conditions *n/b* ratios of 2.2–3.2 are observed for the hydroformylation of octene-1 at 120 °C and 200 psig of CO/H_2. Conversions in the range of 5–25% were observed. Maximum activity with DPPETS occurs at a P/Rh ratio of 3/1; at high P/Rh ratios, catalysts derived from the monodentate water-soluble ligand, TPPTS, are more active.

Several chelating water-soluble phosphines have been reported in the literature. These include the sulfonated phosphines (2-sulfonatophenyl)bis((diphenylphosphino)ethyl)amide and related compounds (**1**)[1] and tetrasulfonated-BDPP (**2**),[2] -chiraphos (**3**),[2] -prophos (**4**),[2] and -cyclobutaneDIOP (**5**),[2] as well as sulfonated BISBI (**6**)[3] and the maleic acid diphosphine (**7**).[4]

Phosphines **1-5** were designed for the preparation of water-soluble hydrogenation catalysts, including asymmetric hydrogenation catalysts. The ligand BISBI is used commercially in propene hydroformylation,[5] and its water soluble-derivative, **6**, was prepared for water-soluble hydroformylation applications.[3] Phosphine **7** was prepared as an alternative to formation of water-soluble phosphines by incorporation of a sulfonate group. However **7** undergoes a variety of reactions in water, including facile oxidation in the presence of nickel salts, which may hinder its use in the preparation of water-soluble coordination compounds; the first phosphine in the series above forms eight-membered rings when chelated to transition metals.

Incorporation of amine groups into the chiral chelating phosphines BDPP, chiraphos, and DIOP provides an alternative to sulfonation for the preparation of water-soluble versions of these ligands.[6] The amine-quaternized form of the ligands form water-soluble transition metal complexes.

The sulfonated phosphines, **2-6**, are prepared by the direct sulfonation of the parent ligand.[2,3] The sulfonation reactions lead to some oxidation of the phosphine; also it is difficult to achieve the tetrasulfonated product.[2,3] Although chromatographic methods have been reported for the separation of mono-, di-, tri-, and tetrasulfonated versions of **2-5**,[7] the ligands are more typically used as a mixture of sulfonated products. The tetrasulfonated derivatives are most easily prepared with the 1,4-diphosphines followed by the 1,3- and the 1,2-diphosphines. Pure tetrasulfonated **4** was only prepared as the dioxide. Not only is BISBI difficult to sulfonate on all four of the phenyl rings but the biphenyl portion of the phosphine is also partially sulfonated.[3]



In general, for chelating phosphines of the type bis(diphenylphosphino)X, which have four phenyl rings to be sulfonated, tetrasulfonation with concomitant partial oxidation still leads to the formation of three compounds; tetrasulfonated bis(phosphine), tetrasulfonated bis(phosphine) oxide, and tetrasulfonated phosphine–phosphine oxide. With careful control of sulfonation conditions, formation of the last two compounds can be minimized.

For many applications in catalytic and coordination chemistry, it would be desirable to have a simple water-soluble chelating phosphine that is well characterized. The prototypical chelating phosphine is bis(diphenylphosphino)ethane, DPPE, and a water-

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soluble derivative of this ligand would be of interest. Information reported on the chiral chelating phosphines, **2-5**, demonstrates that the least substituted phosphine, **5**, is the most difficult to sulfonate.[2] This suggests that DPPE will be even more difficult to sulfonate. However DPPE is comparatively inexpensive and can be sulfonated on a larger scale than that possible with the chiral phosphines.

Here we report the synthesis and characterization of tetrasulfonated DPPE, DPPETS (**8**), and describe some of its coordination chemistry. The transition metal complexes Ni(CO)$_2$DPPETS (**9**), Pd(DPPETS)Cl$_2$ (**10**), Pt(DPPETS)Cl$_2$ (**11**), Rh(DPPETS)$_2$ (**12**), and [Rh(COD)(DPPETS)]Cl (**13**), are described. For comparison with other work in the field of water-soluble phosphines, the ligand is used in the rhodium-catalyzed hydroformylation of octene-1.

Experimental Section

All manipulations and syntheses were performed under prepurified argon or nitrogen using standard Schlenk techniques. THF and pentane were distilled from sodium benzophenone ketyl. CH_2Cl_2 was dried and deoxygenated by distillation from P_2O_5 under nitrogen prior to use. In-house-deionized water and methanol, ethanol, and acetone from Fisher Scientific were deoxygenated by distillation under inert gas prior to use. 1,2-Bis(diphenylphosphino)ethane (DPPE) and oleum (fuming sulfuric acid; 18–24% SO_3) were obtained from Aldrich and used without further purification. Sodium hydroxide was purchased from Mallinckrodt AR. Hydrochloric acid (36%) was received from Fisher Scientific and used as supplied. Ni(CO)$_4$ was received from Alfa Chemicals. Pd(PhCN)$_2$Cl$_2$, Pt(PhCN)$_2$Cl$_2$, Rh(acac)(CO)$_2$, and Rh$_2$(COD)$_2$Cl$_2$ were purchased from Strem Chemical Co. The deuterated solvent D_2O was obtained from Cambridge Isotope Laboratories, and the water-soluble chemical shift standard sodium 3-(trimethylsilyl)tetradeuteriopropionate (TSP) was received from Wilmad Glass Co. NMR measurements were performed on a Bruker WP200 spectrometer at 200.133 MHz for ^{1}H, 50.323 MHz for ^{13}C, and 81.015 MHz for ^{31}P. Infrared spectra were recorded on a Nicolet 5DXB FTIR in 0.1-mm Irtran cells. The standard deviations of the repeated measurements are ±0.1 cm^{-1}. Potentiometric measurements were carried out using a Microcomputer pH Vision, Cole-Parmer Model 05669-20 and a standard Ag/AgCl electrode purchased from Fisher. Elemental analyses of compounds **8-11** gave satisfactory C, H analyses when the level of solvation was taken into account. Solvation was estimated by integration of the solvent protons in the ^{1}H NMR spectra of the compounds. Solvation is well-known in sulfonated phosphines and their complexes.[8,9] Compounds **12** and **13** were isolated with small quantities (ca. 5%) of unidentified phosphorus-containing compounds and were not subjected to elemental analysis.

Key to NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; asterisk, pseudo. Carbon atoms in the phosphine are numbered from the CH_2– group as (1)C and continued with the α-carbon (ipso) on the phosphorus atom labeled (2)C–P through the γ-SO_3Na attached (4)C. Key to IR data: vs, very strong; s, strong; w, weak.

For the catalytic work the CO/H_2 (1/1) was received from Airco and used without further purification. The high-pressure catalytic reactions were carried out in stainless steel 30-mL reaction vessels equipped with appropriate high-pressure gauges. Reaction products and starting materials were determined by gas chromatography on a Varian 3300 chromatograph equipped with an HP1 column, 25 m × 0.32 mm × 0.52 mm, and FID detector; He was the carrier gas; the temperature program was from 50 °C (3 min) to 200 °C (5 min), at a heating rate of 10 °C/min. An Omega CN 2000 temperature process controller was used for the temperature control of the silicon oil bath of the catalytic reactions. The stirring rate was determined by a Lutron Photo-tachometer.

Catalytic Reactions. To ensure good reproducibility in the series of catalytic reaction, separate stock solutions of Rh(acac)(CO)$_2$, 0.015 M in methanol, and DPPETS, 0.100 M in water, were prepared. The components of the catalytic reactions, 0.6 mL of octene-1 (3.8 mmol), 0.51 mL of rhodium stock solution (0.0076 mmol of rhodium), and the appropriate volume of DPPETS stock solution, were combined at room temperature in a 30-mL reactor under CO. Nonane, 0.34 mL, was added as an internal standard for the GC analysis. The reaction vessel was closed, pressurized with CO/H_2 (1/1), and then placed in a silicon oil bath preheated to the reaction temperature, 120 °C. In all reactions, the stirring rate was kept at the same value, 360 rpm. The pressure at reaction temperature was 200 psig. After the appropriate reaction time, the reactor was removed from the oil bath, cooled to room temperature, and depressurized. The products were immediately analyzed by gas chromatography.

To facilitate mixing of the aqueous and nonaqueous phases 0.5% by weight of dodecylbenzenesulfonic acid, sodium salt, was added to each reaction mixture. In a separate series of experiments, the surfactant concentration was varied from 0.5 to 10% by weight, with no effect on product yields or selectivity.

Synthesis of 1,2-Bis[di(*m*-sodiosulfonatophenyl)phosphino]ethane (8). DPPE (10.0 g, 0.025 mol) was added slowly to 125 mL (2.83 mol) of oleum (18–24% SO_3) at 0 °C with vigorous stirring. The mixture was kept at 0 °C for approximately 8 h. The reaction was monitored by ^{31}P NMR; thus, 1-mL aliquots were taken every 24 h by pipet and transferred to a small Schlenk vessel. This small sample was chilled and neutralized slowly with 25% NaOH under intensive stirring. Methanol (25 mL) was added, and the mixture refluxed for 10 min and then filtered hot to removed the Na_2SO_4. The filtered solution was vacuumed dry and analyzed by ^{31}P NMR.

When the desired tetrasulfonated product was present in the greatest concentration compared to phosphine oxides, the reaction was quenched by addition of 25% NaOH at 0 °C to a pH of 8.5. The volume of the neutralized solution was reduced to about 200 mL, and 800 mL of methanol was added. After refluxing for 1 h, the solution was filtered hot, and the salt was washed with an additional portion of hot methanol/water, 4/1, to recover any remaining phosphine. The combined extracts were distilled to dryness. The product was fractionally crystallized from methanol/water, 10/1. Purity, as judged by NMR, was >95%. Further purification can be achieved by precipitation from water by the addition of acetone. The final product, a white crystalline solid, was obtained in 30% yield based on DPPE.

^{1}H NMR $\delta(D_2O)$: 2.31 (t, J_{PH} = 4.8 Hz, 4H, (1)CH_2), 7.49 (d*, J_{HH} = 7.8 Hz, 8H, (6)CH + (7)CH), 7.81 (t*, J_{HH} = 4.2 Hz, 4H, (5)CH), 7.87 (s br, 4H, (3)CH). ^{13}C NMR $\delta(D_2O)$: 25.37 (s, (1)CH_2), 140.67 (t, J_{CP} = 5.8 Hz, (2)C–P), 137.70, (t, J_{CP} = 7.4 Hz, (3)CH), 145.64 (s, (4)C–SO_3Na), 132.15 (t*, (5)CH) + (7)CH), 128.85 (s, (6)CH). ^{31}P NMR $\delta(D_2O)$: –12.45.

Synthesis of Ni(CO)$_2$(DPPETS) (9). DPPETS (0.17 g, 0.2 mmol) was dissolved in 0.5 mL of water, and 2.2 mL of a solution (0.1 M) of Ni(CO)$_4$ in THF was added slowly to the phosphine solution at room temperature with vigorous stirring. Argon was bubbled through the mixture during the addition in order to remove the CO. The color of the reaction mixture changed to a pale yellow. After 1 h, ^{31}P NMR and IR spectra were consistent with the presence of **9** as well an intermediate, a nickel tricarbonyl dimer with a bridging DPPETS between two Ni centers. After 24 h, only the desired product was present and the solvent was removed under vacuum. The pale yellow crude product was dissolved in 0.5 mL of water, the solution was filtered, and the product was precipitated with 10 mL of acetone. The final product, a light yellow powder (yield: 88% based on DPPETS), was filtered off and dried under vacuum.

^{1}H NMR $\delta(D_2O)$: 2.52, 2.61 (2 × s br, 2 × 2H, (1)CH_2), 7.61 (t, J_{HH} = 7.8 Hz, 4H, (6)CH), 7.85 (t*, 8H, (5)CH) + (7)CH), 8.09 (d*, 4H, (3)CH). ^{13}C NMR $\delta(D_2O)$: 27.56 (s, (1)CH_2), 139.64 (t, J_{CP} = 15.3 Hz, (2)C–P), 137.22 (t*, (3)CH), 145.6 (d*, (4)C–SO_3Na), 132.24 (d*, (5)CH), 129.52 (s, (6)CH), 131.21 (t, J_{CP} = 9.1 Hz, (7)-CH), 202.28 (s, CO). ^{31}P MNR $\delta(D_2O)$: 48.47. IR $\nu_{CO}(D_2O)$: 1953.9 (vs), 2010.1 (s) cm^{-1}.

Synthesis of Pd[DPPETS(H)]Cl$_2$ (10). A CH_2Cl_2 solution of Pd(PhCN)$_2$Cl$_2$ (2.0 mL, 0.08 g, 0.2 mmol) was added to a solution of DPPETS(H) (acid form of DPPETS) (0.16 g, 0.2 mmol) in 2 mL of water at room temperature, with vigorous stirring. After 1 h, the water phase was slightly yellow. The aqueous phase was separated from the mixture, washed twice with 5 mL of pentane to remove the residual organic solvent, and reduced in volume under vacuum to 1 mL. Precipitation of the white product was effected by the addition of 15–20 mL of ethanol. The product was filtered off and dried (yield: 92% based on DPPETS). Recrystallization can be accomplished in ethanol/water (20/1).

^{1}H NMR $\delta(D_2O)$: 2.86 (t, J_{PH} = 12.4 Hz, 4H, (1)CH_2), 7.45 (q*, J_{HH} = 5.8 Hz, 4H, (7)CH), 7.68 (t*, J_{HH} = 7.7 Hz, 4H, (6)CH), 7.85 (t*, J_{HH} = 5.1 Hz, 4H, (3)CH), 7.99 (d*, J_{HH} = 8.0 Hz, 4H, (5)CH). ^{13}C NMR $\delta(D_2O)$: 31.15 (t*, (1)CH_2), 138.90 (s, (2)C–P), 133.99 (s br, (3)CH), 147.47 (s, (4)C–SO_3Na), 133.45 (s br, (5)CH) + (7)CH), 131.67 (s, (6)CH). ^{31}P NMR $\delta(D_2O)$: 61.21.

Synthesis of Pt[DPPETS(H)]Cl$_2$ (11). A yellow solution of Pt(PhCN)$_2$Cl$_2$ (0.17 g, 0.2 mmol) in 2 mL of CH_2Cl_2 was added to a solution of DPPETS(H) (0.16 g, 0.2 mmol) in 2 mL of water at room temperature, with vigorous stirring. After 1 h, the reaction was complete and the two colorless phases were separated. The aqueous layer was washed twice with 5 mL of pentane and reduced to a volume of 1 mL. The white solid product was precipitated with 15–20 mL of ethanol, filtered off, and vacuum-dried (yield: 92% based on DPPETS).

^{1}H NMR $\delta(D_2O)$: 2.62 (t, J_{PH} = 12.3 Hz, 4H, (1)CH_2), 7.38 (q*, 4H, (7)CH), 7.56 (t*, J_{HH} = 7.8 Hz, 4H, (6)CH), 7.73 (s br, 4H, (3)-CH), 7.83 (d*, J_{HH} = 7.8 Hz, 4H, (5)CH). ^{13}C NMR $\delta(D_2O)$: 31.27 (t*, (1)CH_2), 139.14 (s, (2)C–P), 133.89 (s, (3)CH), 147.36 (s, (4)C–SO_3Na), 133.60 (s, (5)CH + (7)CH), 131.95 (s, (6)CH). ^{31}P NMR $\delta(D_2O)$: 52.97 (t, J_{PtP} = 2310 Hz).

Characterization of Rh^I(DPPETS)$_2$ (12). A solution of DPPETS (0.17 g, 0.2 mmol) in 2 mL of water was added to Rh(acac)(CO)$_2$ (0.03 g, 0.11 mmol) dissolved in 2 mL of methanol at room temperature with stirring. Argon was bubbled through the reaction mixture to remove generated CO. After 1 h, the solution was taken to dryness under vacuum. The crude product was dissolved in water, the solution was filtered, and the filtrate was reduced in volume to 1 mL. After the addition of 15–20 mL acetone, a yellow oil formed, which was separated from the mixture and vacuum-dried at 40 °C. The solid residue was treated with 15–20 mL acetone, and the mixture was stirred until a fine yellow crystalline precipitate was formed, typically 5–24 h. The product was collected by filtration (yield: 83% based on DPPETS).

^{1}H NMR $\delta(D_2O)$: 2.34 (t br, J_{PH} = 11.6 Hz, 8H, (1)CH_2), 7.51 (d*, 16H, (6)CH + (7)CH), 7.81 (d*, 16H, (3)CH + (5)CH). ^{13}C NMR $\delta(D_2O)$: 31.45 (s, (1)CH_2), 139.88 (s, (2)C–P), 132.41 (s, (3)CH), 145.85 (s, (4)C–SO_3Na), 130.72 (s, (5)CH + (7)CH), 131.07 (s, (6)CH). ^{31}P NMR $\delta(D_2O)$: 60.71 (d, J_{RhP} = 132.7 Hz).

Characterization of [Rh^I(COD)(DPPETS)][Cl] (13). A solution of DPPETS (0.17 g, 0.2 mmol) in 10 mL of THF/water, 4/1, was added dropwise to $Rh_2(COD)_2Cl_2$ (0.054 g, 0.11 mmol) dissolved in 10 mL of THF/water, 4/1, at room temperature with stirring. After 1 h, the solution was vacuum-dried. Water, 2 mL, was added to the crude mixture, and the solution was filtered to remove the small excess of unreacted $Rh_2(COD)_2Cl_2$. The solution was reduced in volume to 0.5–1 mL. Precipitation of the yellow product was effected by the addition of 15–20 mL of ethanol. The product was filtered off and dried (yield: 96% based on DPPETS).

^{1}H NMR $\delta(D_2O)$: 2.45 (s br, 12H, 2 × (1)CH_2 + 4 × CH_2(COD)), 5.07 (s, 4H, CH(COD)), 7.72 (t*, J_{HH} = 7.6 Hz, 4H, (6)CH), 7.84 (t*, J_{HH} = 9.8 Hz, 4H, (7)CH), 8.02 (d br, J_{HH} = 7.8 Hz, 4H, (5)CH), 8.23 (d br, J_{HH} = 10.9 Hz, 4H, (3)CH). ^{13}C NMR $\delta(D_2O)$: 32.05 (s, 2 × (1)CH_2 + 4 × CH_2(COD)), 105.91 (s, CH(COD)), 131.27 (s, (6)CH), 133.69 (s, (3)CH + (5)CH + (7)CH), 137.66 (s, (2)C–P), 146.01 (s, (4)C–SO_3Na). ^{31}P NMR $\delta(D_2O)$: 59.24 (d, J_{RhP} = 151.7 Hz).

Results

The sulfonation of DPPE leads to a complicated mixture of meta-sulfonated products. However, careful monitoring of the reaction allows the sulfonation to be terminated when the maximum yield of tetrasulfonated DPPE is present. The ^{31}P NMR spectra recorded on aliquots taken during the sulfonation are presented in Figure 1. In the inset an expanded view of the phosphine region of the spectrum is given. The highlighted peak is assigned to DPPETS; the signal due to DPPETS typically represents about 55% of the total phosphorus by integration.

Fractional crystallization leads to an isolated yield of up to 30% DPPETS. The product is judged to be completely free of phosphine oxide, as determined by ^{31}P NMR. The product is also free from di- and trisulfonated products, as judged by ^{1}H NMR. The ^{1}H and ^{31}P NMR spectra are shown in Figure 2. Once isolated, DPPETS is relatively stable toward oxidation.

Trisulfonated tris(ω-phenylalkyl)phosphines form stable phosphonium salts in water at pH ≤7–10.5, depending on the phosphine, as determined by potentiometric titration.[8] DPPETS shows no evidence for phosphonium ion formation in this pH range. The titration curve of DPPETS is given in Figure 3. The inflection at pH 6.6 is assigned to different phenylsulfonato groups

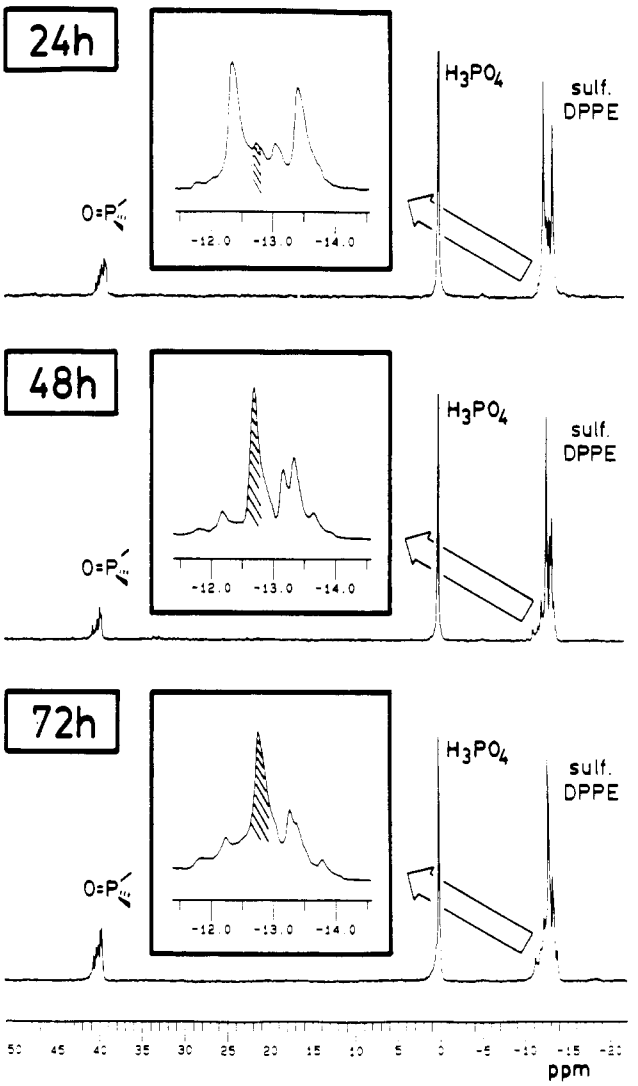

Figure 1. ^{31}P NMR spectra, in D_2O, of aliquots taken from the reaction mixture as described in the Experimental Section. The highlighted signal in the expanded region of the spectrum is assigned to DPPETS. After 3 days this comprises about 55% of the total phosphorus in the sample.

bound to the same phosphorus atom. A similar effect is seen in the titration of trisulfonated triphenylphosphine, TPPTS.[8]

The transition metal complexes **9-13** are all prepared in high yield in water. Isolation of the compounds is accomplished by addition of a water-miscible organic solvent, such as acetone or ethanol, to force precipitation of the solids. A summary of the reactions of DPPETS is shown in Scheme 1. Appropriate NMR data for the new compounds are given in the Experimental Section. Typical are the NMR spectra for **11** in Figure 4. Platinum-195 satellites are observed in the ^{31}P NMR spectrum (J_{Pt-P} = 2310 Hz). This value is unusually small for cis complexes of platinum and may indicate that sulfonated chelating phosphines are more sterically demanding than their nonsulfonated analogs.[10] Alternatively, the complex may contain Pt(IV) due to oxidative addition of HCl. In the ^{1}H NMR spectrum all four protons on the sulfonated phenyl ring are resolved, and the pattern is consistent with meta sulfonation.

The results from the rhodium-catalyzed hydroformylation of octene-1 with DPPETS are summarized in Figure 5. For

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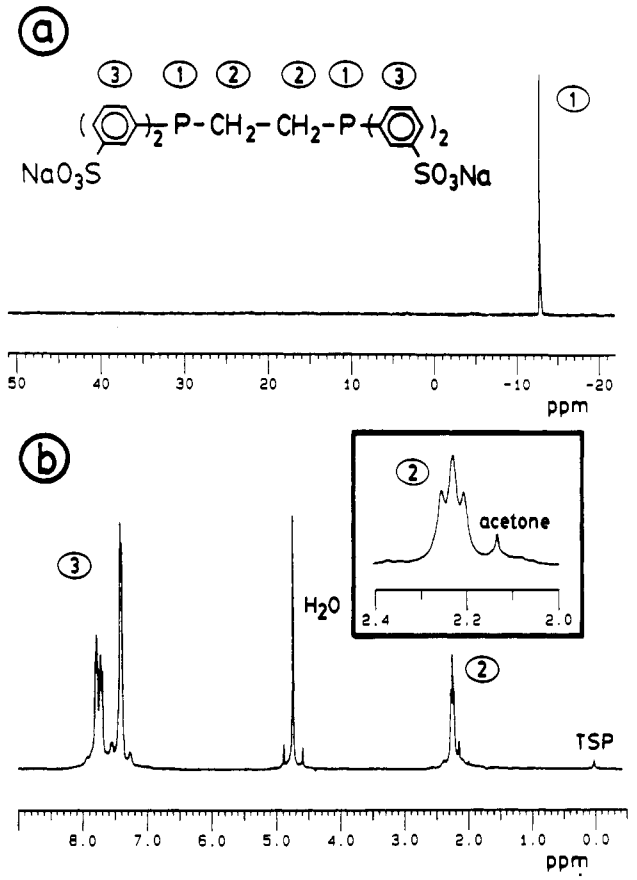

Figure 2. ^{31}P and ^{1}H NMR spectra (spectra 2a and 2b, respectively) for pure DPPETS in D_2O. Within the signal to noise limitations of the spectrometer the sample is free of oxide and all partially sulfonated products. The ^{1}H NMR spectrum is consistent with exclusively meta sulfonation. The larger than normal residual water peak is due to water of crystallization in the sample. The method of preparation, i.e. precipitation from water with acetone, leads to the incorporation of a small quantity of acetone as seen in the inset in spectrum 2b.

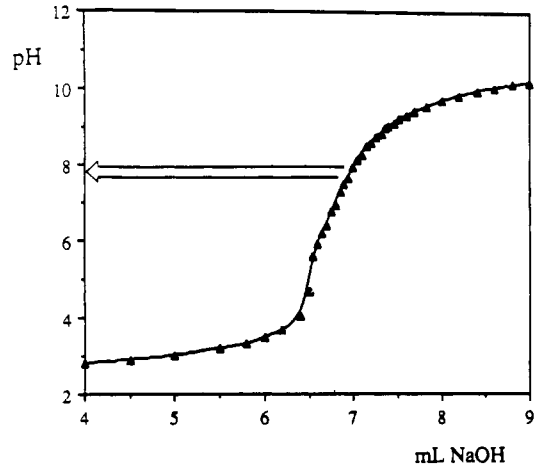

Figure 3. Potentiometric titration of DPPETS. The equivalence point is nearly identical to that observed for TPPTS.

comparison, the results obtained with TPPTS as the water-soluble phosphine are shown as well.[11] When compared at similar conversion of octene-1 and at the same P/Rh ratio, the reaction selectivity (*n/b*) obtained with **8** is nearly identical to those obtained with TPPTS as the water-soluble phosphine although the apparent reaction rate (i.e. conversion over a fixed reaction time) is generally slower with the chelating water-soluble phosphine. The results obtained here with TPPTS are consistent with those previously reported in the literature from several laboratories under a variety of conditions.[11,12]

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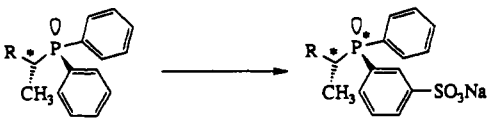
Discussion

As noted by Sinou, Bakos, et al., partial sulfonation of chiral phosphines in which the chiral center is not the phosphorus atom leads to a new chiral center at the phosphorus.[2] This is shown schematically as follows. With the disphosphines **2-5**, this leads to the formation of diastereomers.



In principle, the generation of a new chiral center could alter the optical yield of a catalytic process. It has been shown that the substituents on an achiral phosphorus bonded to a chiral auxiliary can play an important role in determining the enantioselectivity of organometallic reactions. For example, in a series of nickel complexes of the phosphorus(III) compounds, P(O-menthyl)R_2, the optical yield obtained in the synthesis of 3-methyl-(*E*)-4-hexen-2-one showed a strong dependence on the nonchiral groups R.[13] Surprisingly small differences in R (R = Me/Et, Ph/CH_2Ph, etc.) could even reverse the sense of chirality of the product.

In the case of the sulfonated chiral phosphines, **2-5**, careful chromatographic separation of the tetrasulfonated phosphines followed by fractional crystallization from aqueous methanol allowed a comparison to be made between a tetrasulfonated derivative and a mixture of its partially sulfonated analogs.[2] It was noted that there is a small difference in enantioselectivity for the asymmetric hydrogenation of cinnamic acid derivatives, depending on the degree of sulfonation.[2]

The examples above illustrate the importance of the purity of the sulfonated chiral phosphines in determining optical yields in catalytic reactions. The sulfonation of DPPE, like the sulfonation of other diphosphines, leads to a complicated mixture of products. Significantly, in the present case, pure tetrasulfonated product can be isolated by fractional crystallization and precipitation. Since the sulfonation of DPPE appears to be more difficult than sulfonation of the chiral phosphines, **2-5**, it is likely that tetrasulfonated chiral phosphines may be also isolated in high purity by similar methods.

Sulfonation of triphenylphosphine to yield TPPTS generates a water-soluble phosphine that is less electron donating than triphenylphosphine.[8] This is attributed to the inductive effect of the electron-withdrawing sulfonato groups. Tetrasulfonated DPPE (**8**) also is expected to be less donating than DPPE. Evidence for this is seen in the infrared data in the carbonyl region for (DPPE)$Ni(CO)_2$[13] and **9**. The former has bands at 1998 and 1936 cm^{-1}, while its water-soluble analog, **9**, has bands at 2010 and 1954 cm^{-1}.

The synthesis of **9** is accomplished via a reaction intermediate characterized only in situ by NMR and IR spectroscopy. This intermediate represents a dimer in which one DPPETS ligand bridges between two nickel centers (^{31}P NMR δ = 29.72 ppm, IR ν_{CO} = 2068.7 (m), 2002.0 (vs) cm^{-1}). The reaction of nickel tetracarbonyl with DPPE has been shown to proceed via such a dimer.[14,15]

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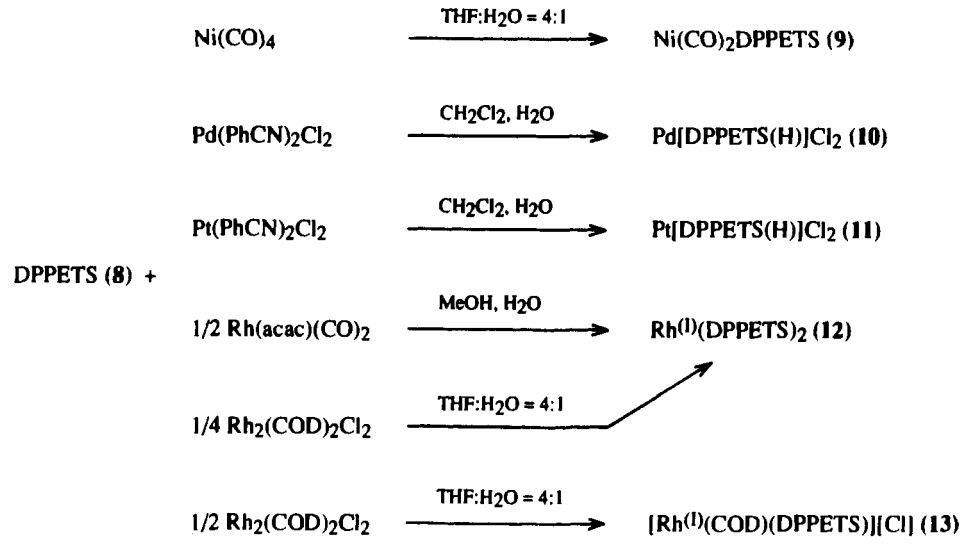
(13) (a) Bartik, T.; Marko, L.; Gerdes, I.; Heimbach, P.; Knott, W.; Schulte, H.-G. *Chirality* **1991**, *3*, 324. (b) Bartik, T.; Gerdes, I. *J. Organomet. Chem.* **1985**, 253.

(14) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 1378.

Scheme 1



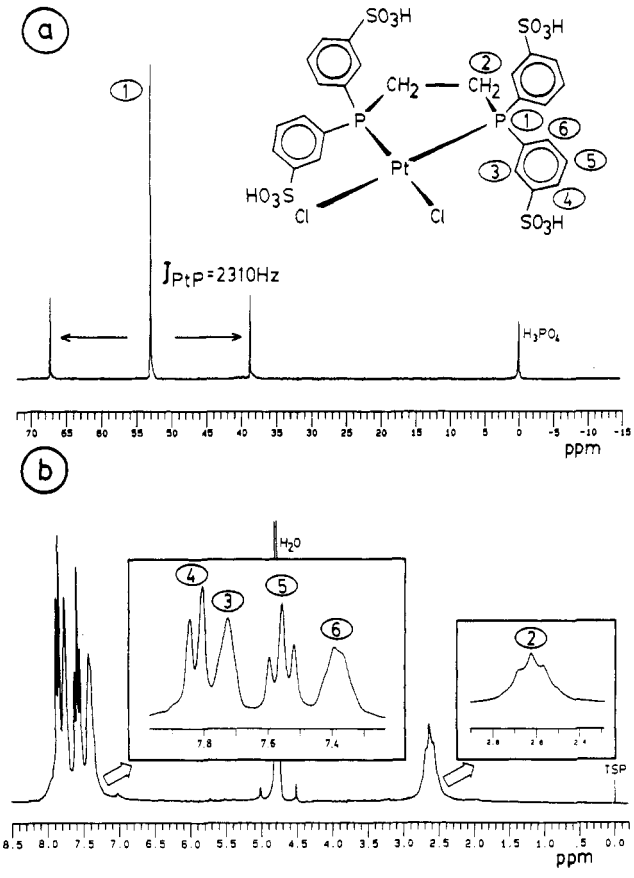


Figure 4. ^{31}P and ^{1}H NMR spectra (spectra 4a and 4b, respectively) for $Pt[DPPETS(H)]Cl_2$ in D_2O/DCl. All four protons of the meta-sulfonated phenyl rings are resolved.

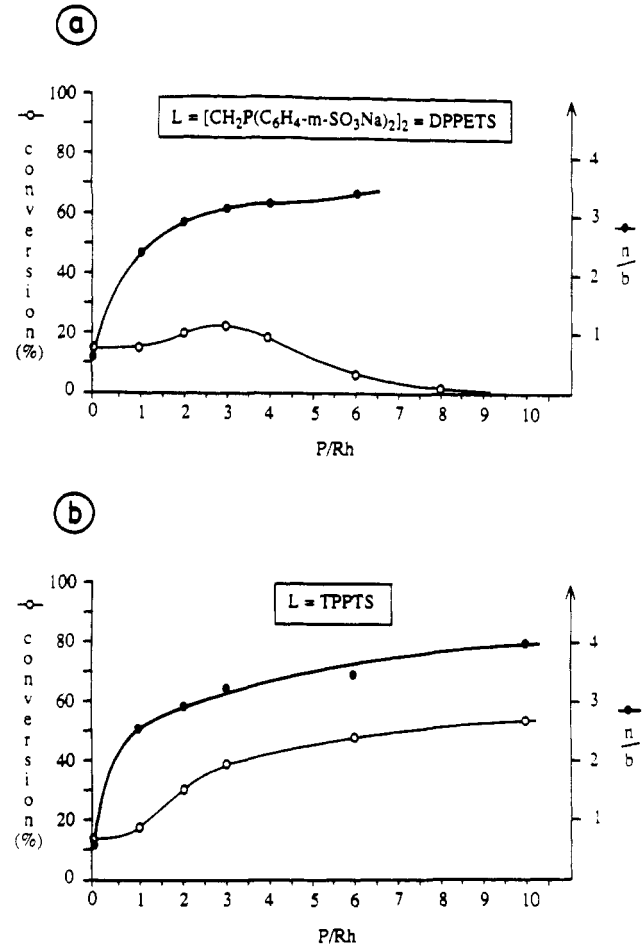


Figure 5. Octene-1 hydroformylation with $Rh(acac)(CO)_2$ and DPPETS (a) and TPPTS (b) as a funciton of P/Rh. Conversion (○) and *n/b* ratio (●) are plotted as a function of L/Rh ratio. Reaction time = 15 h; octene-1/Rh = 500; temperature = 120 °C; pressure = 200 psig.

Compounds **10** and **11** are similar to their nonsulfonated analogs. It is known that chloro complexes of palladium and platinum undergo hydrolysis reactions in water. Compounds **10** and **11** however appear to be stable under the conditions reported in the Experimental Section, that is at low pH. Water-soluble palladium and platinum complexes may find application in olefin hydrogenation reactions.

Interestingly, all attempts to prepare rhodium derivatives of DPPETS from $Rh(acac)(CO)_2$ yielded a compound with two DPPETS ligands bound to rhodium. Compound **12**, which formally contains Rh(I), is cationic if one ignores the charge on the sulfonato groups. All efforts to generate and detect a hydride failed to give any evidence in support of the presence of a hydride ligand. It is possible that a sulfonato group from one of the DPPETS ligands weakly coordinates the rhodium. If this is the case, then the compound may be considered to be zwitterionic in the sense that the counterion to the Rh(I) center is part of the same complex. With $Rh(acac)(CO)_2$ as the starting material a

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complex containing just one DPPETS ligand could not be prepared. In contrast with $Rh_2(COD)_2Cl_2$ as the starting material, compound **13** could be prepared under homogeneous reaction conditions (Scheme 1); with excess DPPETS, or under two-phase reaction conditions, compound **12** is formed. The ^{31}P NMR spectra of **12** and **13** compare well with those of their nonsulfonated analogs.[16,17]

The hydroformylation of octene-1 with **8** and $Rh(acac)(CO)_2$ is instructive with respect to the mechanism of hydroformylation in the aqueous phase. At high P/Rh ratios, it is likely that compound **12** forms, and this is inactive for hydroformylation, since it is unlikely to provide an open coordination site at the metal by dissociating one chelate ligand. At relatively low P/Rh ratios, the rate is also slower with **8** than with TPPTS although the reaction selectivities are comparable. It has been suggested previously that the ability to form trans intermediates is significant for the generation of active and selective rhodium hydroformylation catalysts. The hydroformylation of olefins in the presence of chelating phosphines has been examined extensively to determine this facet of the mechanism.[18-21] Generally, *n/b* ratios are low with chelating phosphines,[19,20] which is attributed to a higher rate of olefin isomerization as well as an inherently lower propensity for anti-Markovnikov addition to the terminal olefin with the chelating phosphines.[20] With the water-soluble chelate DPPETS, we observe *n/b* ratios nearly identical to those obtained with TPPTS (Figure 5). This suggests that the inherent selectivity as determined by the sense of addition to the terminal olefin is the same for DPPETS as for TPPTS.

Other chelating ligands have been observed to give both good rates and selectivity in the hydroformylation of olefins. The chelate BISBI forms seven-membered chelate rings and thus may be able to approximate a trans arrangment of phosphines; very high *n/b* ratios are obtained with BISBI.[3,5] Chelating phosphites are also observed to give good rates and selectivity.[21] Recently, a binucleating tetradentate chelating phosphine was shown to give excellent selectivity for the hydroformylation of higher olefins.[22]

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